A new technology to manufacture polypropylene foam sheet and biaxially oriented foam film

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Abstract

Foamed polymers are future materials with their wide application spheres. They can be used to enhance appearance as insulating structures or to save material costs. This study addresses all of these and concerns a new technology to produce foamed tubes and films. An entire blown film extrusion line was built up to fulfil the final target, biaxially oriented foam film with closed cell, microcellular foam structure.

Extrusion conditions, which in general means temperature, pressure and flow control of viscoelastic material, is discussed and examined experimentally to define the dominating characteristics. Screw and die design together with foam stabilisation is taken under stringent examination, resulting a three layer blown film die focused for foamed extrudates.

The effects of chemical foam nucleating agents and physical and chemical foaming are examined during the study concluding in formation of cell embryos by chemical foaming agents and expanding them into low density foam with physically compressed nitrogen gas. The effect of processing parameters in foam structure is examined and adapted according to the polypropylene.

The main characteristics of polypropylene were defined by rheological measurements to promote foaming studies in extrusion. Sharp melting point and linear structure of polypropylene caused troubles in keeping the foam structure closed during expansion, but was also partly resolved with new bimodal type polypropylene owing to high melt strength properties.

Some applications, leading to new commercialised innovations in foam films, will also be discussed in greater detail.

Preface

The experimental procedure of this study was carried out in the Institute of Paper Converting at Tampere University of Technology (TUT). The composition of this study was further completed in the Technical Research Centre of Finland (VTT).

I wish to express my deepest gratitude to my supervisor, Professor Antti Savolainen for all the professional criticism that I needed to be motivated to finish this work.

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Tampere, April 1998   Jaakko Raukola

Contents

Abbreviations

ΔG^*_{hom}	Gibbs free energy for homogenous nucleation
ΔG^*_{het}	Gibbs free energy for heterogenous nucleation
γ_{bp}	surface energy on gas bubble/polymer interface
ΔP	gas pressure inside a foam cell
$S(\theta)$	contact angle between a pareticle nucleator and gas
ΔG_{hom}	change in Gibbs free energy for homogenous nucleation
ΔG_{hom}	change in Gibbs free energy for heterogenous nucleation
ΔG	Gibbs free energy
Cr_n	nucleation rate
CLS	critical limiting supersaturation
GBD	growth by diffusion
RSN	rapid self nucleation
S	saturation
ΔF	system free energy
σ	surface tension
A	interfacial area
Δp	pressure difference
r	bubble radius
p_g	gas pressure
k	Henry´s law constant
c_w	mass fraction gas at the bubble surface
D	diffusion coefficient
D_o	diffusion coefficient (material dependent)
E_D	activation energy in diffusion
R	ideal gas law constant
T	temperature
p_L	external pressure
A*	Hamaker constant
a	average length
δ	wall thickness
CFC	fluorocarbon
PS	polystyrene
PP	polypropylene
γ_a	apparent shear rate
γ_w	shear rate on wall

Q	volumetric flow rate
w	slit width
h	slit thickness
τ_w	shear stress
P_{exit}	exit pressure
J_e	elastic compliance
τ_{11}, τ_{22}	normal stress
$\overline{M}_w$	weight-average molecular weight
$\overline{M}_n$	number-average molecular weight
$\overline{M}_z$	z-average molecular weight
$\overline{M}_{z+1}$	z+1-average molecular weight
EMF	electro mechanical film
MWD	molecular weight distribution
PTFE	polytetrafluoroethylene
POM	polyoxymethylene
PET	polyester
G'	dynamic storage modulus
G''	dynamic loss modulus
L/D	length to diameter
T_g	glass transition temperature
$\overline{V}$	volumetric flow
PE	polyethylene
NOPP	nonoriented polypropylene
OPP	oriented polypropylene
BOPP	biaxially oriented polypropylene
CTM	cavity transfer mixer
UC	Union Carbide
d	capillary diameter
MD	machine direction
TD	transverse direction
T_{mc}	melt temperature
T_D	die temperature
P_m	melt pressure
P_g	gas pressure
P_b	film blowing pressure
n_1, n_2, n_3, n_4	speed of rotation
F_b	buoyant force

m	weight
ρ	density
MFR	melt flow rate
T_m	melting temperature
T_c	crystallization temperature
M	molecular weight
PI	polydispersity index
DSC	differential scanning calorimetry
MFI	melt flow index
BUR	blow up ratio
CFA	chemical foaming agent

1. INTRODUCTION

The use of polymer foams in today's world has constantly increased. Many reasons support this growth: light weight, insulation properties, softness, excellent strength/weight ratio, material costs, energy absorption performance etc. Many times reductions after foaming in material costs are around 30 % without compromising the function or required strength, which is one of the advantages that could lead to even wider use of foams in industry. The chemicals used are today environmental friendly and the mechanical and barrier properties can be greatly affected by multilayer constructions; mechanically strong sandwich structures can be produced with solid skin layers, low gas permeability polymers and tie layers support their use for high barrier packages.

The main applications for foamed plastics can be found in the building, automobile, packaging and sport industries. They include the end products for insulative sheets, floor coverings, profiles for finishing, automobile linings, packaging films, cable wires, interior finishing, shoes and cups.

Because of environmental demands, foamed polymers have also been threatened and raw material and process manufacturers have been forced to find solutions for recyclable polymers, more flame and temperature resistive structures and alternatives for blowing agents' deleterious effects on the ozone layer. These challenges have led studies more away from the traditional materials, polystyrene and polyurethane and towards the use of polyolefins, polyethylene and polypropylene [1, 2, 20, 43].

The use of polymeric foams in sandwich structures is also cheaper compared to honeycomb structures and does not increase the weight of the structure. Solid surfaces can be cohesively bonded to the foamed core, which simplifies the processing [65].
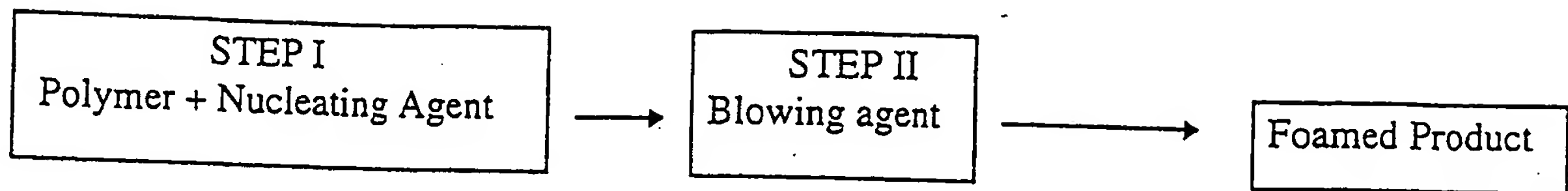
2. THEORIES

2.1 The Formation of Foam Structure in Polymers

A foamed polymer can be understood as a structure of two phases; gas and polymer. To make the phases in a uniform, homogenous order a third solid component, the nucleator, is significant.

Foaming methods can be divided into chemical and physical foaming. In chemical foaming chemical nucleating agents are added in melt polymer and foaming gas is produced by decomposition of the nucleator at a certain temperature (Figure 1). In physical foaming the polymer, which has a small amount of nucleating agents is saturated with external gas, the foaming agent.

Polymer foaming is introduced in the literature mainly as a batch process, where nucleating agents are mixed with the polymer, which is separately saturated with gas below the glass transition temperature (T_g) under high pressure. A supersaturated specimen is produced when pressure is reduced. When the specimen is now heated again above the glass transition temperature, the foam cells nucleate spontaneously. Cell growth is under control due to the glassy polymer, which is slowly heated. This gives a good basis for studies of cell formation and growth. Most of the studies are more concentrated on chemistry and nucleation theories of polystyrene with batch process instead of process technology of foamed continuously extruded polyolefins. In high pressure batch foaming the foam extent is high and densities less than 0.1 g/cm^3 can easily be reached. Fine microcellular foam structure can be achieved and the diameter of the bubbles is less than 20 μm [10, 19, 20, 27]. Batch foaming is commonly used for low density foamed products with a certain shape. The advantages are high foam extent, microcellular closed cell structure and high mechanical strength. For commercial applications the pressure to supersaturate the semifinished product is high, which increases the costs of the process. Foaming in two steps, temperature control and typically slow diffusion phenomenon encountered are resulting in low cycle times.

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┌─────────────────────────────┐      ┌──────────────────┐                ┌──────────────────┐
│         STEP I              │      │     STEP II      │                │  Foamed Product  │
│ Polymer + Nucleating Agent  │ ───▶ │  Blowing agent   │ ─────────────▶ │                  │
└─────────────────────────────┘      └──────────────────┘                └──────────────────┘
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Figure 1. The principle of batch foaming.

In continuous foaming chemical nucleating agent is mixed with polymer and extruded. The extrudate expands immediately after the pressure drop, after die exit [16, 44]. The processing temperature area is narrow and the foam structure easily collapses due to the almost explosive reaction of chemical foaming agents and often quite low processing viscosity. With physical foaming, gas compression into the extruder, the density of the products can be decreased more, and also the cell growth control becomes more feasible [1, 16]. Continuous foaming is normally simply one stage extrusion, where the temperature is kept below the polymer melting point (Figure 2). The development of endothermic nucleating agents has assisted the control of the expansion to a continuous foam product. Extrusion is widely used and foam bubbles easily grow larger than 100 μm in diameter.

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        STEP I
┌─────────────────────────────┐                          ┌──────────────────┐
│ Polymer + Nucleating Agent +│ ───────────────────────▶ │  Foamed Product  │
│ Blowing agent               │                          │                  │
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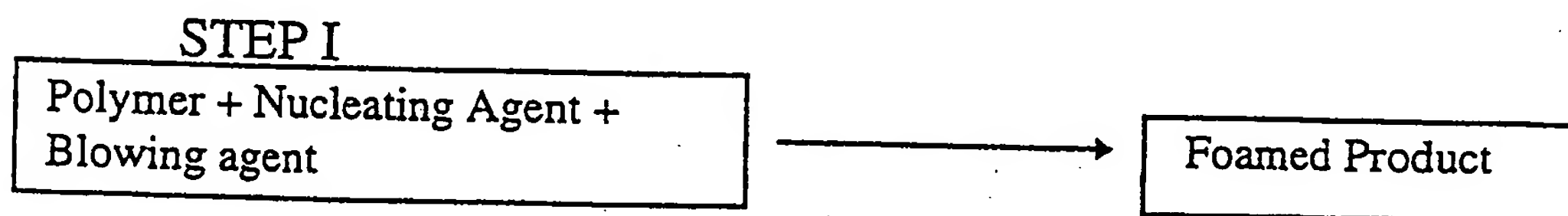
Figure 2. The principle of continuous foaming.

The formation of foam structure can be illustrated as a three stage process, where

a) foam cells are created as a result of chemical reaction of the nucleating agents or as a result of gas dissolved into the polymer - bubble nucleation.

b) foam cells grow as a result of external pressure drop and diffusion of the gas from the polymer into the foam bubble at increased temperature - bubble growth.

c) foam structure is balanced by cooling the structure - foam stabilisation.

The use of the terms foam bubble and foam cell is introduced in the literature sometimes inconsistently many times with the same meaning. In this study a general distinction is made and foam cell is discussed when unstabilized foam embryos is considered. When the foam cell is stabilised, it is considered to be a foam bubble. Sometimes this distinction is still unsatisfactory.

The quality of the final foam structure is affected not only by foaming parameters but also by the polymer morphology and rheology as well as foaming agents and foam nucleating agents, all of which will be introduced in this study.

2.1.1 Foam Nucleation

A foam cell can be generated in a polymer by
- self-nucleation, when nucleation occurs as a result of gas dissolved in homogenous polymer phase

or

- heterogeneous nucleation with nucleators, where chemical nucleators produce gas by decomposition. Solid particle nucleators can also be used, but a foaming agent is needed, i.e. externally dissolved foaming gas in polymer.

Self-nucleation generally causes troubles in foam control. The foam structure includes large foam bubbles which are far apart from each other. Heterogeneous nucleation is more homogenous and foam bubble formation occurs at low gas concentrations [2, 3, 40]. The activation energy barrier (1), (2) introduced by Colton & Suh is much lower in heterogeneous nucleation compared to selfnucleation. In mixed mode nucleation processes, where both nucleation types are present, the heterogeneously activated cells still grow larger in diameter, because they appear first and gas diffusion starts in the cells before the self-nucleated ones. Figure 3 illustrates the Gibbs free energy

change, which seems energetically to favour heterogeneous nucleation [4, 5, 6].

Gibbs free energy for homogenous nucleation is as follows

$$\Delta G^*_{hom} = 16\pi\gamma_{bp}^3/(3\Delta P^2), \tag{1}$$

where

γ_{bp} = surface energy of the foam bubble polymer interface
ΔP = pressure of the gas in the cell

Gibbs free energy for heterogeneous nucleation can be introduced as

$$\Delta G^*_{het} = \Delta G^*_{hom} \bullet S(\theta), \tag{2}$$

where $S(\theta)$ depends on the wetting angle of the third phase. $S(\theta)$ is the contact angle between particle nucleator and gas and it receives values less than 1.

Nucleation formation and cell growth have been examined in self nucleation foaming and is introduced in Figure 4. The result can also be applied for heterogeneous foaming to explain foam generation.
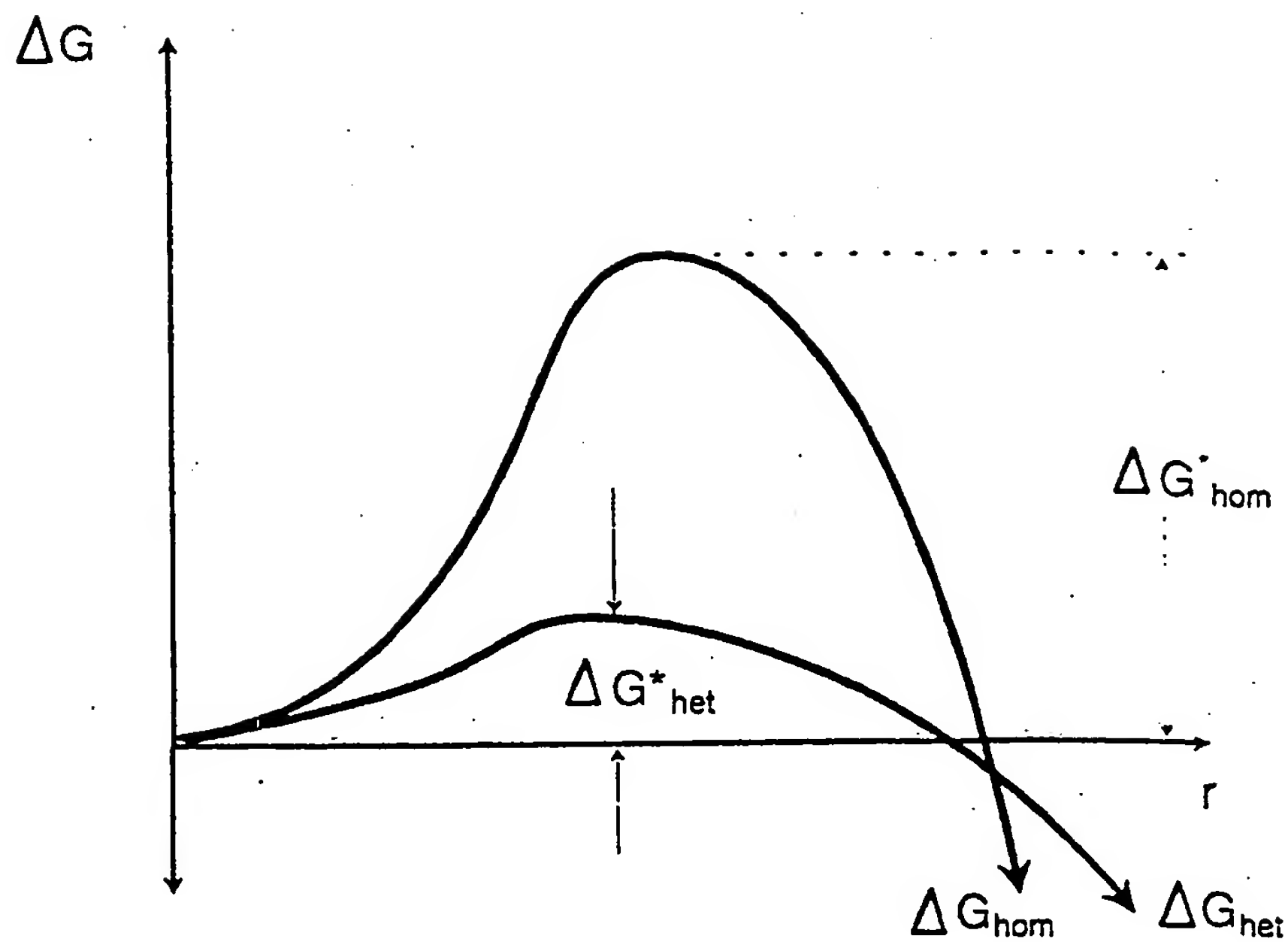
Figure 3. Gibbs free energy for self and heterogeneous nucleation [5].

r = *bubble radius*

ΔG = *Gibbs free energy*

ΔG_{hom} = *Gibbs free energy for homogenous nucleation*

ΔG_{het} = *Gibbs free energy for heterogeneous nucleation*

ΔG^*_{hom} = *change in Gibbs free energy needed to create a critical homogenous nucleus*

ΔG^*_{het} = *change in Gibbs free energy needed to create a critical heterogeneous nucleus*

Figure 4. An illustration of gas concentration in solution, nucleation and growth of foam cells [2].

Cr_n = nucleation rate
CLS = critical limiting supersaturation
GBD = growth by diffusion
RSN = rapid self nucleation
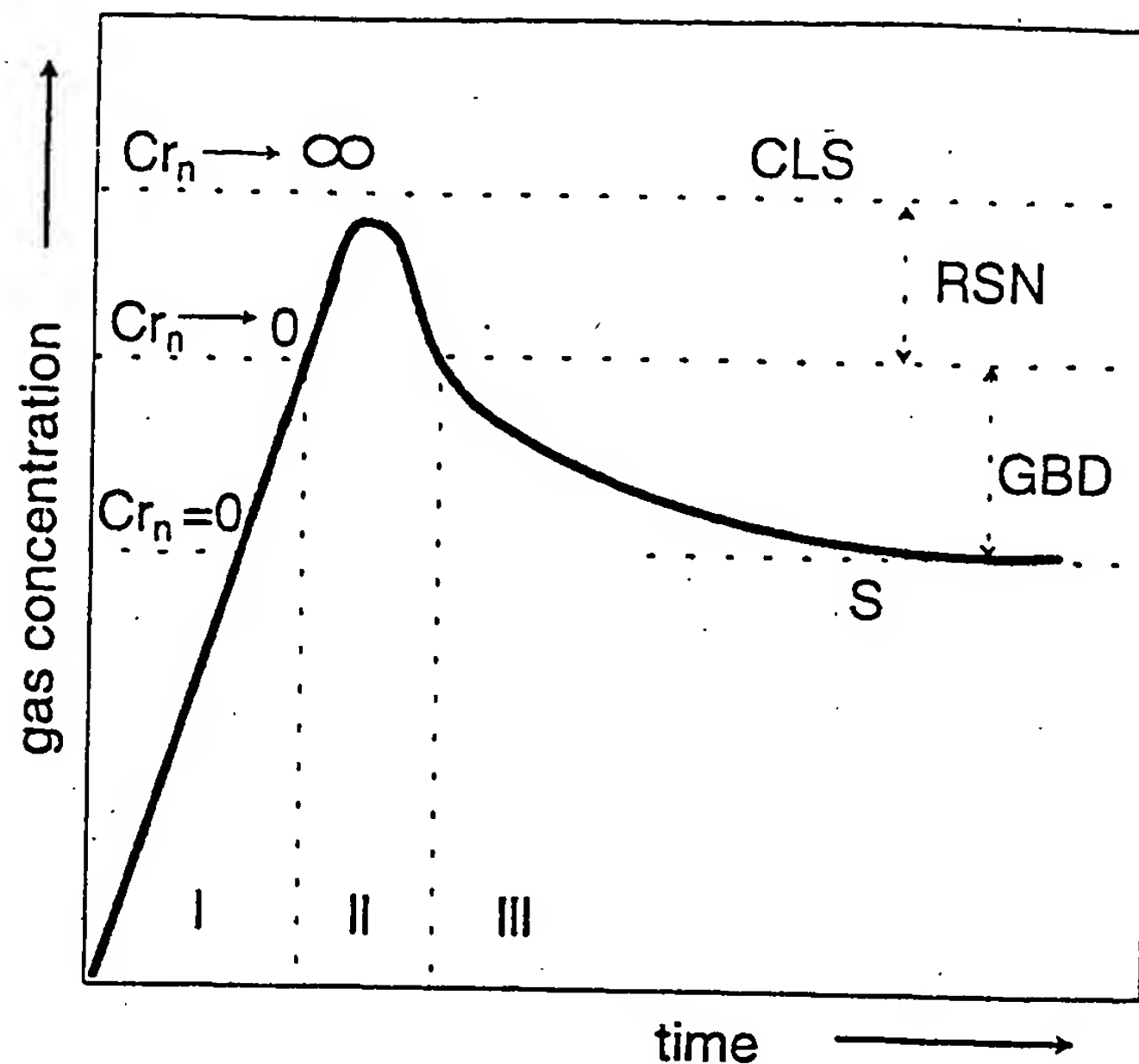S = saturation

In sector I the gas concentration increases until it exceeds the saturation concentration. With more gas generation the concentration is reaching the self nucleation level RSN. In the critical concentration point the gas concentration starts to decrease because of the growth of the foam cells and diffusion of the gas. No cells will be formed under the self nucleation level and the existing cells continue their growth in level GBD.

If system includes microvoids or microcells, which can be produced with a chemical foam nucleating agent or another additive, sector II generally disappears. When saturation level has been reached, the gas starts to diffuse into the microvoids. According to the theories and to other studies, there is no clear answer if the nucleation source occurs by self-nucleation or diffusion into the microvoids in an individual bubble [4, 5, 2].

If the system is considered under system free energy (3), the formation of one single cell always increases the system free energy ΔF. Decrease in surface tension lowers the energy needed for bubble formation. On the other hand, tightly packed microcellular foam structure is more unstable compared to sparse big bubbled foam [2].

$$\Delta F = \sigma A, \text{ where} \tag{3}$$

σ = surface tension of the liquid
A = total interfacial area

Another equation which favours the collapse of the foam cells and thus the formation of larger foam bubbles is expressed as follows:

$$\Delta p_{12} = 2\gamma/(1/r1 - 1/r2), \text{ where} \tag{4}$$

r_1 = radius of foam cell 1
r_2 = radius of foam cell 2
Δp_{12} = pressure difference between cells 1 and 2

According to Equation (4) the gas pressure at equilibrium in the smaller cell is higher compared to the larger one favouring the diffusion of the gas into the larger cell.

Increased shear rate breaks the nucleator agglomerates more effectively causing new, smaller nucleators for foam cells. The gas phase from the cavities of the agglomerates are free to form a cell if the agglomerate is broken under high shear [7].

According to Youn et al. [8] and Lee et al. [9], nucleation may also occur from the presence of voids due to nucleator geometry or presence of agglomerates. A small amount of gas is retained in the voids, where the gas dissolved in polymer starts to diffuse.

As Klempner & Frisch [2] and Pham [49] and Isayev et al. [15] have shown, the nucleation can be increased if the process is shocked thermally, mechanically or radially. Many chemical nucleating agents act like "hot-spots", where foam cells nucleate, or the system can be radiated effectively to produce uniform foam structure.

The latest studies by Campbell et al. [56, 57] show an interesting theory for heterogeneous nucleation with highly elastic performance rubber particles which act as microvoids. The saturation pressure can be significantly reduced and the elastic forces oppose the bubble growth leading to smaller bubble size in polystyrene foaming.

2.1.2 Bubble Growth

When the external pressure of the saturated polymer is reduced the foam cells start to grow rapidly. A foam cell appears, when the dissolved gas diffuses to the foam embryos from the immediate radius (r2-r1) of the polymer as Figure 5 illustrates. The bubble growth will be governed by the rate of diffusion of dissolved gas to the polymer-gas interface r1 as well as by the degree of supersaturation and viscosity of the melt.

Effectiveness of the diffusion is heavily temperature dependent and it can be described with Arrhenius´ equation

$$D = D_0 \exp(-E_D/RT), \text{ where} \tag{5}$$

D = diffusion coefficient
D_o = material dependent diffusion coefficient
E_D = activation energy in diffusion
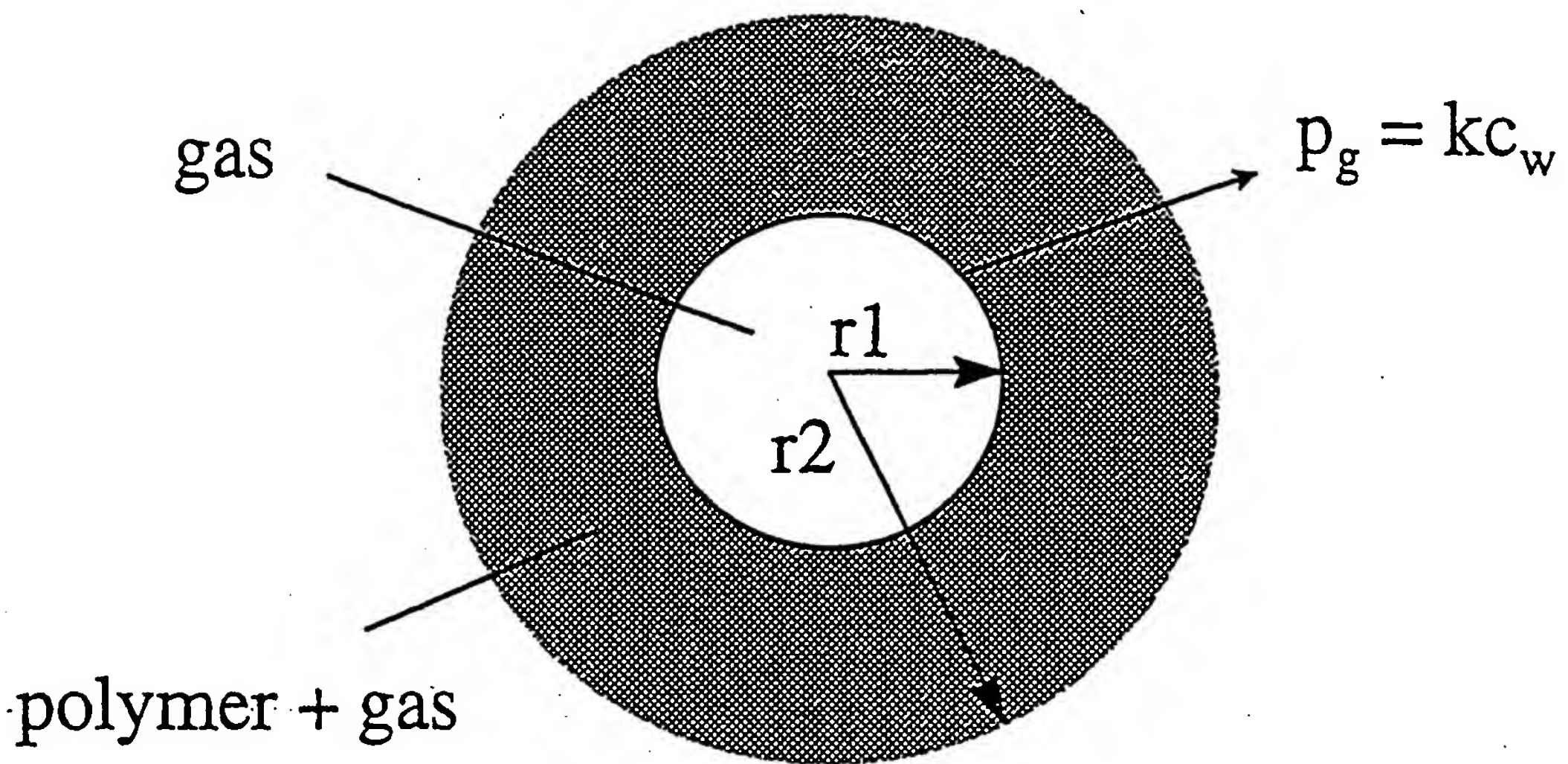R = ideal gas law constant
T = temperature

Figure 5. An illustration of a single bubble and the radius of gas diffusion in polymer[10].
r1 = foam bubble radius
r2 = the radius of polymer/gas mixture, where diffusion occurs
p_g = gas pressure
k = Henry´s law constant
c_w = mass fraction of gas at the bubble surface

The concentration of the gas has almost no effect on diffusion in solid polymers because of low interaction and solubility between gas and polymer. Solubility is considerably increased in molten polymers (in extrusion foaming). Molecular size, shape and reactivity of the gas has a major influence on diffusion [3, 11, 12, 13].

When temperature is increased the viscosity of the polymer decreases and the diffusion of the gas around the foam bubble is accelerated. With low viscosity polymers or at high temperature the expansion of the cells is more complete [9, 19].

The collapsing of the foam bubbles is likely during temperature increase due to elastic behaviour of polymers, which decreases with increased temperature.

According to Han [3], when the saturation pressure is increased, the growth of the foam bubbles is increased, because of the pressure inside the cell seeks equilibrium with the outer gas pressure.

$$\Delta p = 2\sigma/r \tag{6}$$

where
$$p = p_g - p_L$$
p_g = pressure inside the foam bubble
p_L = external pressure in the polymer melt
σ = surface tension of the bubble inner circle
r = radius of the foam bubble

Beckman et al. [58, 59] have shown that the foam bubble size can be decreased by increased saturation pressure in batch foaming with supercritical carbon dioxide. The increase in saturation pressure favours homogenous nucleation and smaller foam bubbles can be achieved. They also showed bigger and fewer cell generation with short saturation time.

In the foaming of molten polymers smaller bubbles can be achieved by heterogeneous nucleation and the increase in saturation pressure leads to increased bubble growth [3].

2.1.3 Foam Stability

Foaming is a common phenomenon when low surface tension liquids are concerned. Foam generally disappears in liquids in the course of time. Main foam theories are still made for liquids, which can also be applied to polymers. Foaming in polymers is more hindered due to their viscoelastic behaviour and the structure can be "frozen" by lowering the temperature.

When deformed cells continue to grow in still molten polymer, the wall of the cell is stretched thin. In the first stage the bubbles formed are circular, but when the foam extent is more than 74 % , the walls of the bubbles change their form and the structure becomes like a honeycomb, which can be examined as a 2-dimensional structure (Figure 6).
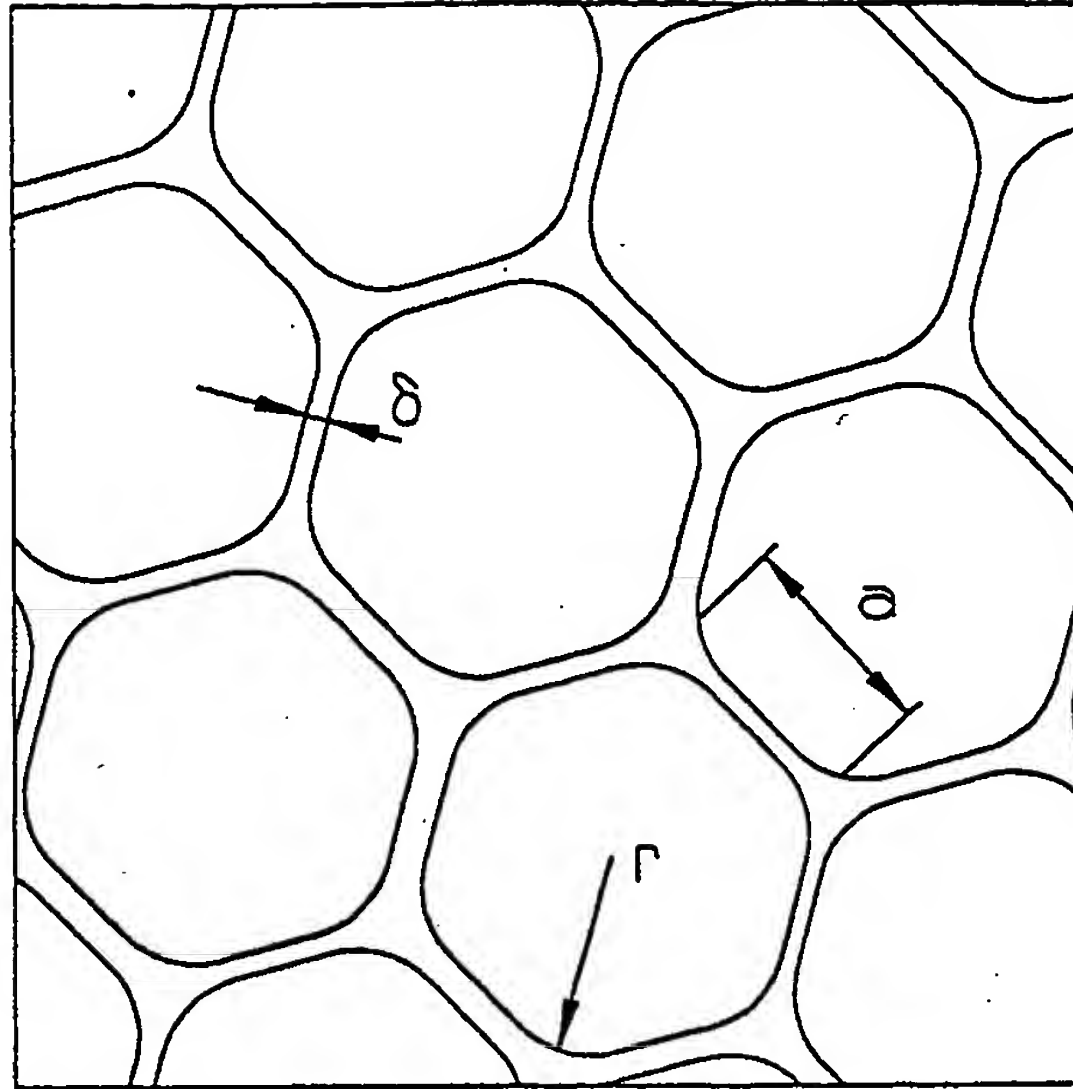
Figure 6. Illustration of a 2-dimensional foam in equilibrium stage [17].

The dimensions of the structure and the amount of polymer phase can be described by the wall thickness δ, the average length a and Plateau corner radius r [17].

$$\sigma/r = A^*/\delta^3 \qquad (7)$$

A* = Hamaker constant

Surface active additives and surface effects play an important role in foam stabilisation . The effect of surface active additives is based on their movement from lower surface energy areas to higher ones during bubble growth. They form a thin interface between foam bubble and polymer. The movement of the surface active additives is flowing (Marangoni effect) or diffusive (Gibbs effect). The growing of the foam bubbles lowers the surface active additive concentration on the surface leading to increased surface tension, which stabilises the foam structure [2, 14, 24, 28].

According to the system free energy (Equation 3) the energy barrier of the cell nucleation can be lowered by lowering the surface tension of the interface between the nucleator and polymer. In three phase polymer foaming the solid particle nucleators should not be wetted by the polymer. If the polymer wets the particle, gas will not create a bubble on the surface. But if the particle is treated with a surface active additive which lowers the interface of particle and polymer, the gas will form a bubble so that the surface active layer spreads along the surface of the growing cell [42].

Besides surface viscosity and Marangoni effect, mutual repulsion of the electric double layer is referred to in the discussions of the relative stability of foam films. Repulsion effects in polymers are more perceptible if very low viscosity polymers and thin bubble walls are considered.

When the growing foam cell comes into contact with a cooled surface the walls of the cells collapse and level out on top of each other forming a solid skin layer. This has been successfully used in structural or integral skin foams. The surface of the structure is smooth and the mechanical properties of the foam are improved. The technology is introduced later in Figure 9 [68].

2.1.4 Foaming Agent

The use of fluorocarbon (CFC) compounds is based on their good solubility in polymers and their effective and stable foaming ability. The use of ozone deleterious CFC- compounds is today prohibited because of European Community norms. In polymer foaming they have also had to be replaced with safer CFC-compounds or with other inert gases such as nitrogen and carbon dioxide [25, 26].

According to Klempner & Frisch [2] mixtures of helium and air are used to control the density of the material better than with 100 % air or nitrogen.

Han [3] showed the effect of polymer melt pressure on solubility of gases at different temperatures. The effect of temperature on solubility is not so dramatic with nitrogen, carbondioxide or air compared to the solubility behaviour of CFC-compounds. The increase of the polymer melt pressure in extrusion foaming cause more complete dissolving of foaming gas in polymer.

The higher the processing pressure is the more gas can be dissolved in the polymer, which furthers high foam extent. This has also been observed by Fehn [16] in the extrusion process.

Solubility and diffusion characteristics of foaming agents in polymers are introduced in the experimental section (Chapter 3.4).

2.1.5 Foam Nucleating Agent

Nucleation agents used in heterogeneous foaming are mainly chemical nucleators and particles. The most widely used are azo-compounds, which decompose exothermally. The processing temperature has to be just above the decomposition temperature of the chemical foaming agent in order to achieve a microcellular foam structure. The increase in the amount of chemical nucleating agent first increases the foaming degree and density of the bubbles affecting more uniform foam structure. If the amount of nucleators is still increased, they quickly destroy the microcellular closed cell structure and the foam bubbles collapse [16].

The advantage of endothermally decomposive bicarbonate and citric acid compounds is their temperature binding effect, which assists in receiving uniform and stabilised foam structure. Their processability in different temperatures is also wider. Exothermic reaction in molten polymers is often problematic, because the reaction goes to the final end when the critical temperature has been reached. Endothermic reaction will only develop in proportion to the amount of heat applied [18, 66].

Mineral particle nucleators, such as calciumcarbonate and talc powders, are widely used in biaxially oriented foam films, which are also called pearlized or cavitated structures. Pearled film is based on orientation process, where the interface around the particles is stretched forming small cavities in the polymer structure (Figure 7). The foam extent of the film is low (density around 0.7 kg/dm^3) but the film becomes highly opaque because of interscratches [21, 22, 23].
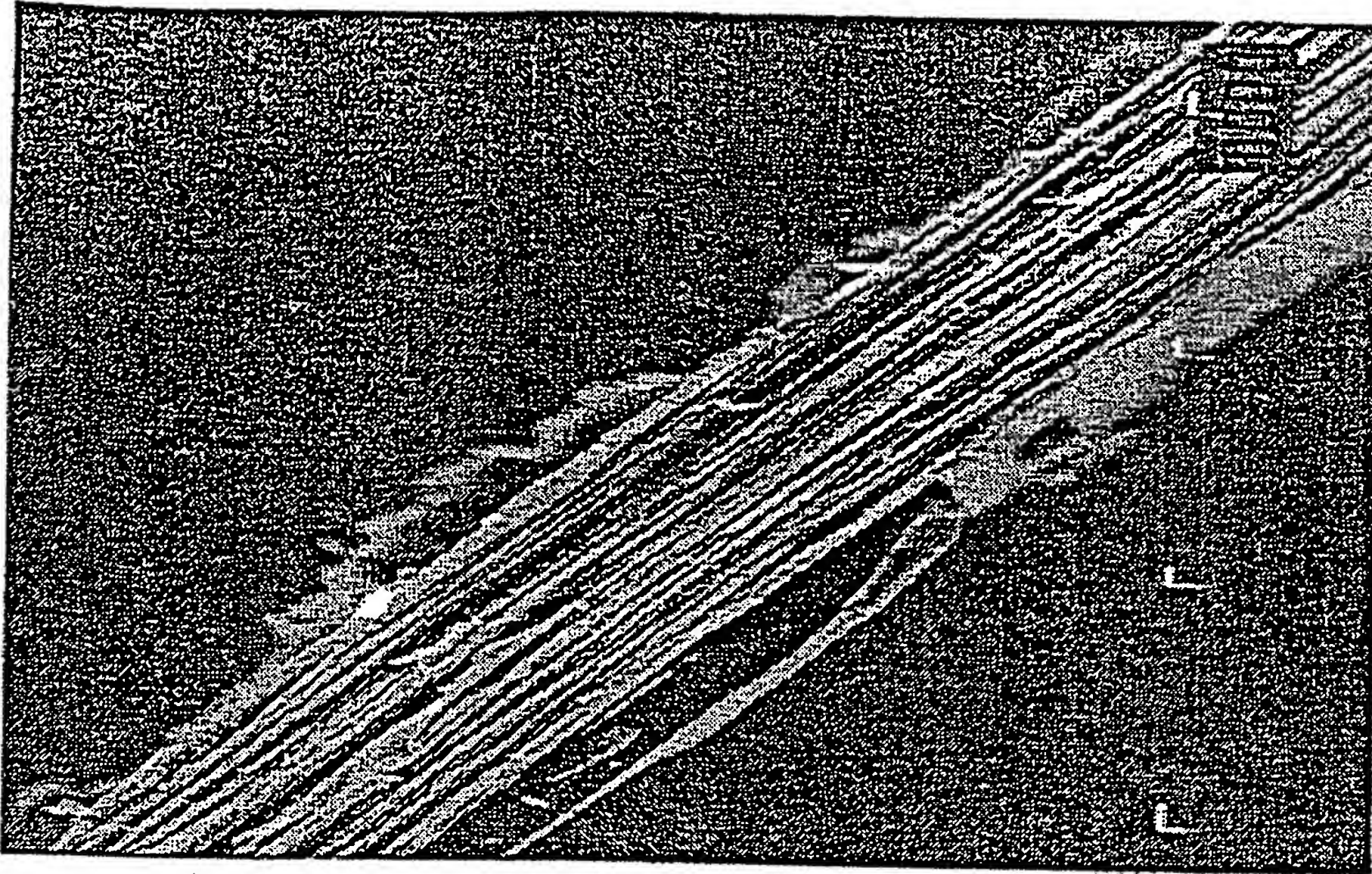
Figure 7. A cross section from biaxially oriented, pearled polypropylene film, interscratches on top of each other. The thickness of the film is 60 μm. (200 X)

2.1.6 Polymer Morphology

In low density foams the walls of the cells are stretched into a very thin honeycomb structure during cell expansion. Cell growth is the most critical stage in foaming and it defines the main demands of the foamed polymer. One of the dominant characteristics in foaming is polymer melt strength or extensional viscosity, which are dependent on polymer morphology, molecular weight distribution and long chain branching. The melt polymer behaviour under stretching should be strain hardening, where extensional viscosity increases in extension. If the walls of the bubbles are stretched by necking, the probability of bubble collapse increases[29, 30, 43].

Viscoelastic properties of polystyrene (PS) are near optimal for a low density foam. The viscosity decrease of amorphous polymers is slow when temperature is increased, and the optimal operating range for foaming is wider compared to crystalline polymers (Figure 8).

The material properties of crystalline polymers can be fixed by changing their molecular structure or by adding another polymer. According to Cogswell [41],

the extensional viscosity of the polymer can be increased by increasing the amount of high molecular weight fraction of molecular weight distribution, which leads to high viscosity and polymer chain entanglement. Altepping & Nebe [45] and Mixon & Stewart [46] have patented their studies, where low density polypropylene foam could be created by blending some high viscosity and low viscosity polypropylenes or polypropylene and low density polyethylene in a certain ratio.
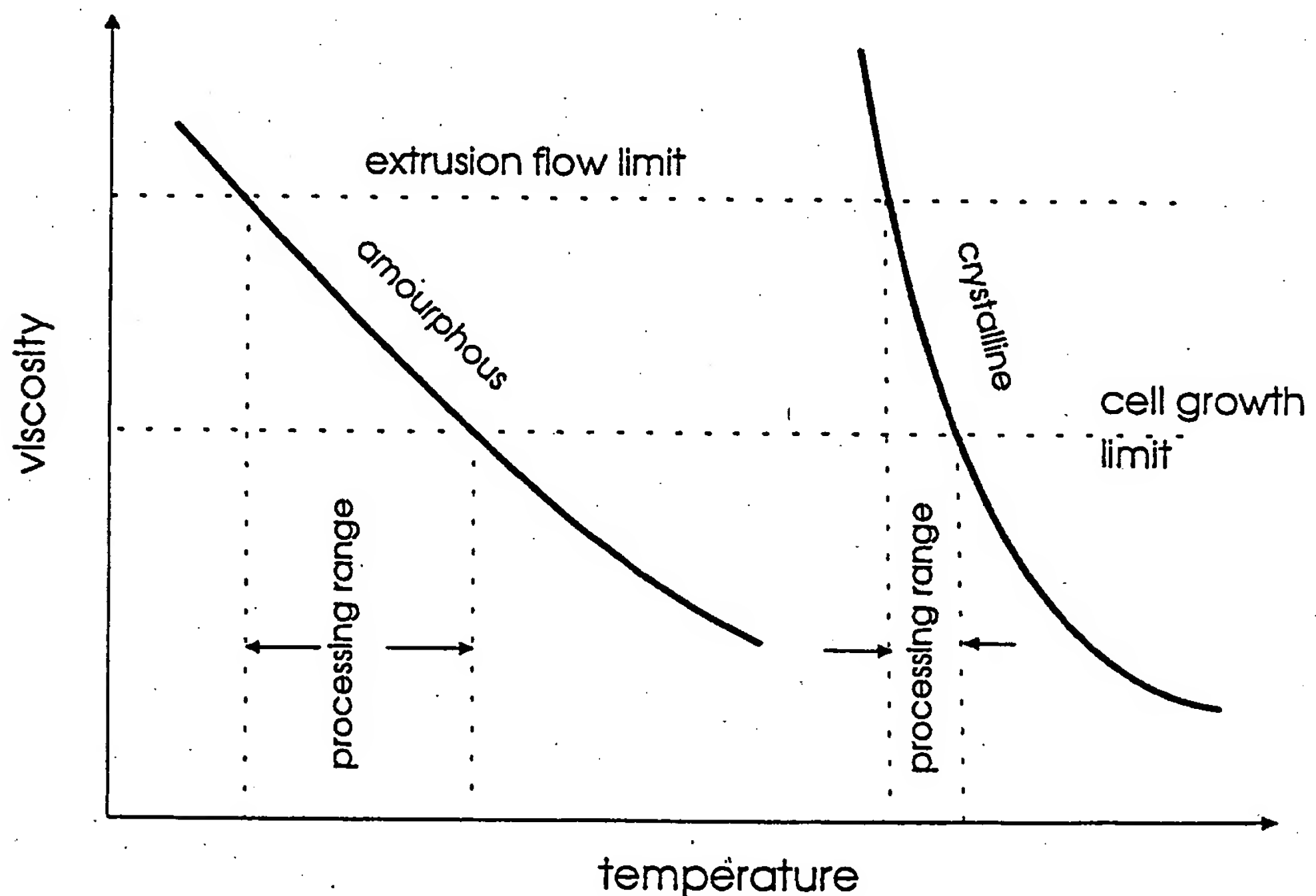

Figure 8. The optimal operating range with amorphous and crystalline polymers [1].

Melt strength is normally understood as a concept which can be numerically measured by extensional viscosity, or elastic compliance even though Kubat et al. [36] have made studies on extensional viscosity where melt strength has been measured numerically.

A bimodal processing method was developed to increase melt strength properties and it was first applied to polyethylene. Besides foaming, high melt strength properties are beneficial in extrusion coating and lamination, where high line speeds and thin coatings are desired. The principle of bimodal process

is to add a controlled region of high molecular weight tail to increase the extensional viscosity of polyethylene. The same technology has subsequently also been adopted in polypropylene [38].

Campbell et al. [10] and Suh et al. [6] have shown, that the increase of polymer molecular weight has no effect on foam bubble density, but it decreases the diameter of the bubbles. The growth of molecular weight does not necessarily cause chain entanglement, only viscosity increases.

According to Hingmann and Marczinke [63] even with a slight long chain branching the elongation properties and tension stiffening of polypropylene are greatly affected.

The extension of bubble walls during foam expansion is biaxial. Uniaxial extension has been studied widely, but because of more complicated stretching, only few studies have been made biaxially. Masuda et al. [60] have shown tension stiffening with broad molecular weight distribution of polystyrene and polypropylene both in uniaxial and biaxial extension.

One possibility to increase the processing window for foaming of crystalline polymers is to crosslink the structure with another polymer or with a crosslinking additive. In crosslinking the viscosity of the polymer increases rapidly and the structure becomes netlike, which prevents the collapse of the bubbles and the diffusion of the gas. The foam structure is more uniform and small bubbled. Peroxides are the most widely used crosslinking additives for polyethylene. For linear or near linear polymers, such as polypropylene, the process becomes more complicated. Linear polymers have to be modified to be non-linear with maleic anhydride and afterwards crosslinked with silane or radiation curing [31, 32].

2.1.7 Rheological Properties of Polymers

As has been discussed in Chapter 1.6 the elastic properties of polymer play the most important role when choosing the polymer for closed cell microcellular foam. Die swell phenomenon is typical for viscoelastic materials and it can be explained by the stored inside elastic energy. One way to measure the stored elastic energy is die exit pressure, which can be extrapolated from the reduction

of pressure in the die. Exit pressures are determined because they can be related to rheological properties such as first normal stress difference and elastic compliance. The quantities can be calculated from exit pressure measurements in a fully developed flow region. Rheological measurements with a slit die are most reliable when shear rate is in the range of 100 - 1000 1/s.

Apparent shear rate γ_a in a slit die is:

$$\gamma_a = 6Q/wh^2, \tag{8}$$

where

Q = volumetric flow rate
w = slit width
h = slit thickness

Shear stress at wall, τ_w:

$$\tau_w = (\partial p/\partial z)h/2, \text{ where} \tag{9}$$

$\partial p/\partial z$ = pressure gradient in the fully developed region

First normal stress difference $\tau_{11} - \tau_{22}$:

$$\tau_{11} - \tau_{22} = p_{exit} + \tau_w (\partial p_{exit}/\partial_w), \text{ where} \tag{10}$$

p_{exit} = exit pressure

Elastic compliance J_e

$$J_e = (\tau_{11} - \tau_{22})/2\tau_w^2 \tag{11}$$

According to Han [33], stored elastic memory increases when the shear rate is increased, which is due to viscoelastic properties of polymers and molecular weight distribution. The effect of shear rate is explained by entanglement of polymer chains, which store more elastic pressure under high shear. Han has also proved that stored elastic memory increases, when temperature decreases.

This is in correlation with increased elastic properties (increased exit pressure) at low temperature of molten polymers [54].

Exit pressure (p_{exit}) increases

- when molecular weight $\overline{M}_w$ is increased, or when molecular weight distribution is wide
- when long chain branching is increased.

Exit pressure and elastic compliance give the base data to determine the elastic properties of polymers with different molecular weight distributions. Rheological measurements have to be done in the fully developed flow region of the die in order to obtain reliable values of p_{exit}. The total L/D value of the die (L = the length of the die, D = the diameter of the die) should be around 140 and the first pressure transducer in the L/D ratio of 30 at minimum [34]. For extrusion rheometer systems even this is not always sufficient for fully developed flow, which has also been examined in literature [38, 64].

It has been shown by Tzoganakis et al. [35] that narrow MWD trends to have low values of extrudate swell and exhibit an extensional viscosity that is almost independent of shear rate. In practice this means that narrow MWD materials will not tend to stiffen under extension and these polymers allow high speed lines in extrusion. If this is compared to studies by Cogswell [41], which illustrate tension stiffening behaviour in branched polymers and shear thinning with linear structures, it has to be remembered that narrow MWD does not necessarily mean linear polymer.

Kraynik [67] studied the rheological properties of foamed thermoplastics in extrusion and found that the foaming pressure i.e. the pressure at the moment cells appear in die is not dependent on flow rate, but depends on the melt temperature and blowing agent concentration. Flow rate effects the residence time of the foam in the tool. If residence time increases, the extent of gas phase will increase resulting in bubble collapse and large-celled foams. This is important when foamed products are made by extrusion and it gives information on locating cooling section (foam stabilisation) in order to gain the finest,

smoothest and uniform foam structure. The optimised situation would be when the foaming starts just after the die exit.

The traditional way to measure rheological properties and to obtain precise data instead of apparent is cone and plate tooling in dynamic shearing. Dynamic storage modulus G' and dynamic loss modulus G'' can be determined from the data to provide information on polymer viscosity and elasticity [41].

2.2 Foam Technologies

Foaming is widely used in injection moulding and mold press to produce low weight and insulative structures for protective applications like helmets, dashboards, protectors and covers. Especially in injection moulding the only aim is often light weight and material saving.

The foam extrusion technologies are mainly for the production of foamed polymer sheets, tubes or profiles. The cooling is made efficient at the surface, which forms a thin solid skin layer to strengthen the profile mechanically. The foam expansion may be free or restricted by a torpedo structure in the die (Figure 9). With the torpedo, it is possible to create a space inside the structure for the foam to expand. Free expansion technology means large swell in profile diameter, but with torpedo the change in diameter is almost zero from the die exit to the stabilised foamed product [1, 2].

Integral foams are widely used in injection moulded products and pipe technology. The main idea is to cool the foam surface rapidly to prevent cell expansion near the outer surface. This guarantees a smooth surfaced product which can replace multilayer structures. Controlled cooling on the outer surface increases the viscosity of the polymer locally, while the inner part keeps the low viscosity, where cell expansion mainly occurs. Foam cells decrease in diameter the closer they get to the surface. Cooling and stabilisation of the foam extrudate is more controllable with a closed die cooling compared to free expansion.
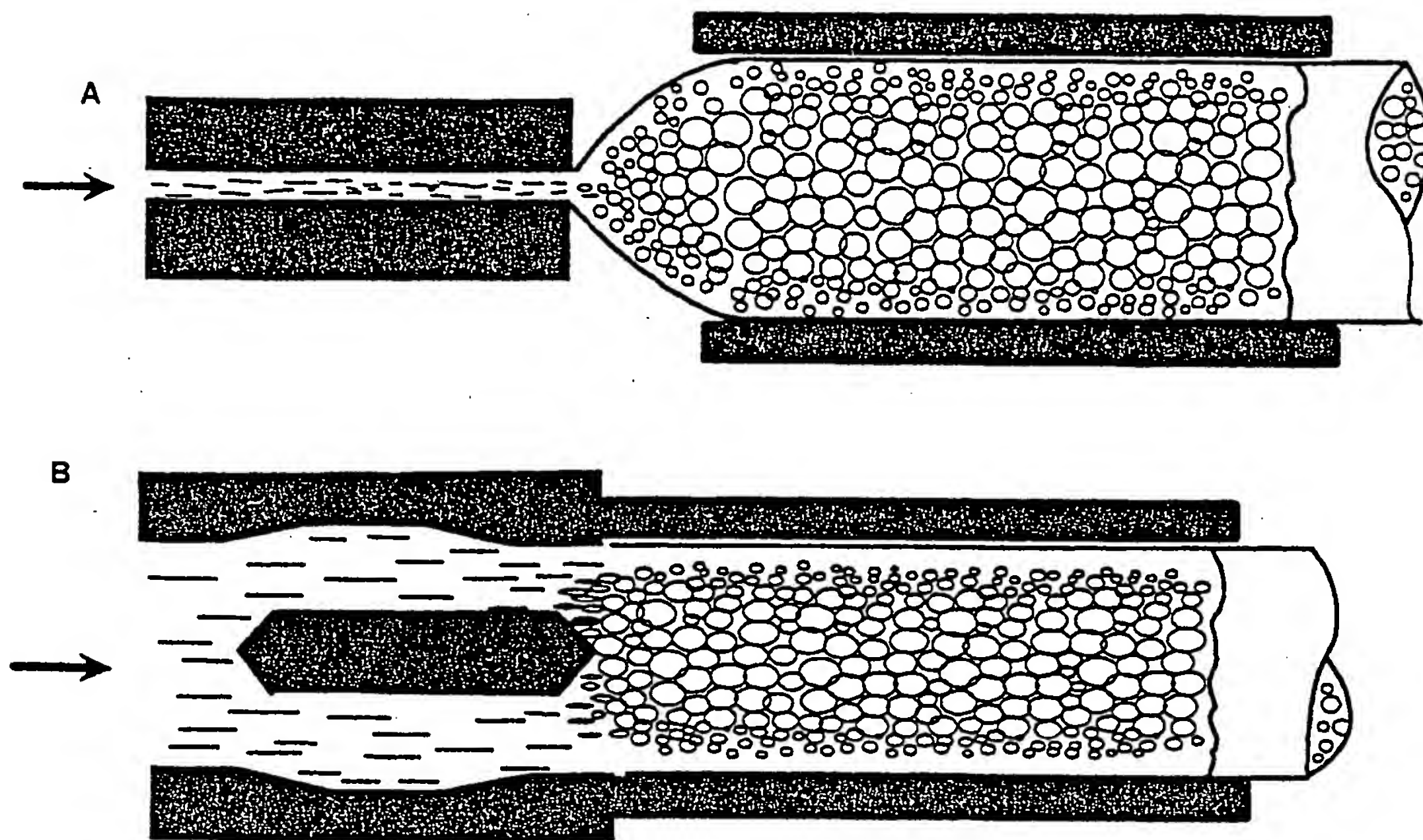
Figure 9. An illustration of bubble formation and foam core distribution in extruded string [2].

      A) Free foam expansion and cooling

      B) Torpedo aided expansion in closed die cooling

Foam extrusion with a flat die is more complicated compared to the rounded profiles and pipes. When the polymer expands after die exit, it expands three dimensionally causing transverse wrinkles. They can be eliminated with a more viscous surface layer or by spreading the slit sheet immediately with a roll. By changing the skin layer thickness the runnability of the sheet can be improved and it is possible to form sandwich structure, where a rigid layer is located at the surface. One practical problem in flat die foam extrusion coating is the nip, where the web is joined to the molten film. Soft foam bubbles of film are flattened under high pressure [47, 48, 61].

A recently published study by Baldwin et al. [69] introduces a method to avoid transverse wrinkling and to gain a fine microcellular foam structure in sheet extrusion. The process is based on independently accomplished three-stages; polymer/gas solution formation, cell formation under pressure and final shape formation. To avoid rapid expansion and uncontrolled bubble collapse and bubble growth after die exit, the pressure is reduced into a certain level where

cell density is high and cell diameter small. After the prefoaming stage the two phase structure is forced into the shaping device, whose temperature is greatly reduced in the die lip area. Reduced temperature increases melt strength of the polymer, decreases the specific volume of the gas phase and increases the surface tension, which all minimise the over expansion of the cells.

2.3 Polypropylene

The most widely used polypropylene grade is the isotactic type, where methyl groups align on the same side of the polymer backbone. Isotactic polypropylene is highly crystalline, which contributes to good stiffness, tensile strength and chemical resistance. Density of the PP is 0.89 - 0.90 g/cm^3 . The basic resin variables are $\overline{M}_w$ and MWD, where $\overline{M}_w$ greatly affects viscosity and MWD in rheological parameters.

Polypropylene is a typical semicrystalline polymer whose melting point and crystallisation point can be determined. Crystalline structure is spherulitic, which is made up of fibrils. Fibrils themselves are made up of crystallites with folded chains. Amorphous material is found between the fibrils and the spherulites [72].

In drawing polymer is elongated at a temperature higher than polymer's melting point, where polymer melt properties such as viscosity, branchness and melt strength are crucial. Molecular orientation then affects the final semicrystalline structure after cooling. [73]

In stretching, polymer is first cooled and reheated above T_g to be stretched and oriented. Under stretching the stress in the amorphous region increases causing slipping. The deformation of the crystalline region occurs by twinning of crystals or slippage of crystal planes. If stretching is extended, tilting, slipping and twisting of lamellas carry on and the fragments orient into microfibrils. The orientation of crystals increases the stiffness and strength of the polymer. Because orientation occurs in the direction of stretching the film anisotropy is greatly increased.

Material development of PP has made it possible to replace polyethylene in foam sheet extrusion. The main advantages are improved thermal and chemical resistance; microwave applications. High melt strength foamed polypropylene sheets can be used for thermoformable packages and for blow moulding. Low density polypropylene foamed pellets are also produced for extensive applications in insulation and sports equipment [51, 52, 53].

Improving melt strength in extrusion by bimodal process has been an epoch-making technology to broaden the applications of PP. Improvements in mechanical properties in molten stage has enabled fast extrusion line speeds with minimised pinholes and also enabled the use for foam applications. Bimodal process was first developed for polyethylene to improve mechanical properties and processability. The properties can be more easily modified into targeted purposes by adding low or high molecular weight fractions in polymer chains. The result is a bimodal molecular weight distribution, where two peaks can be observed instead of the traditional one (Figure 10) [74].
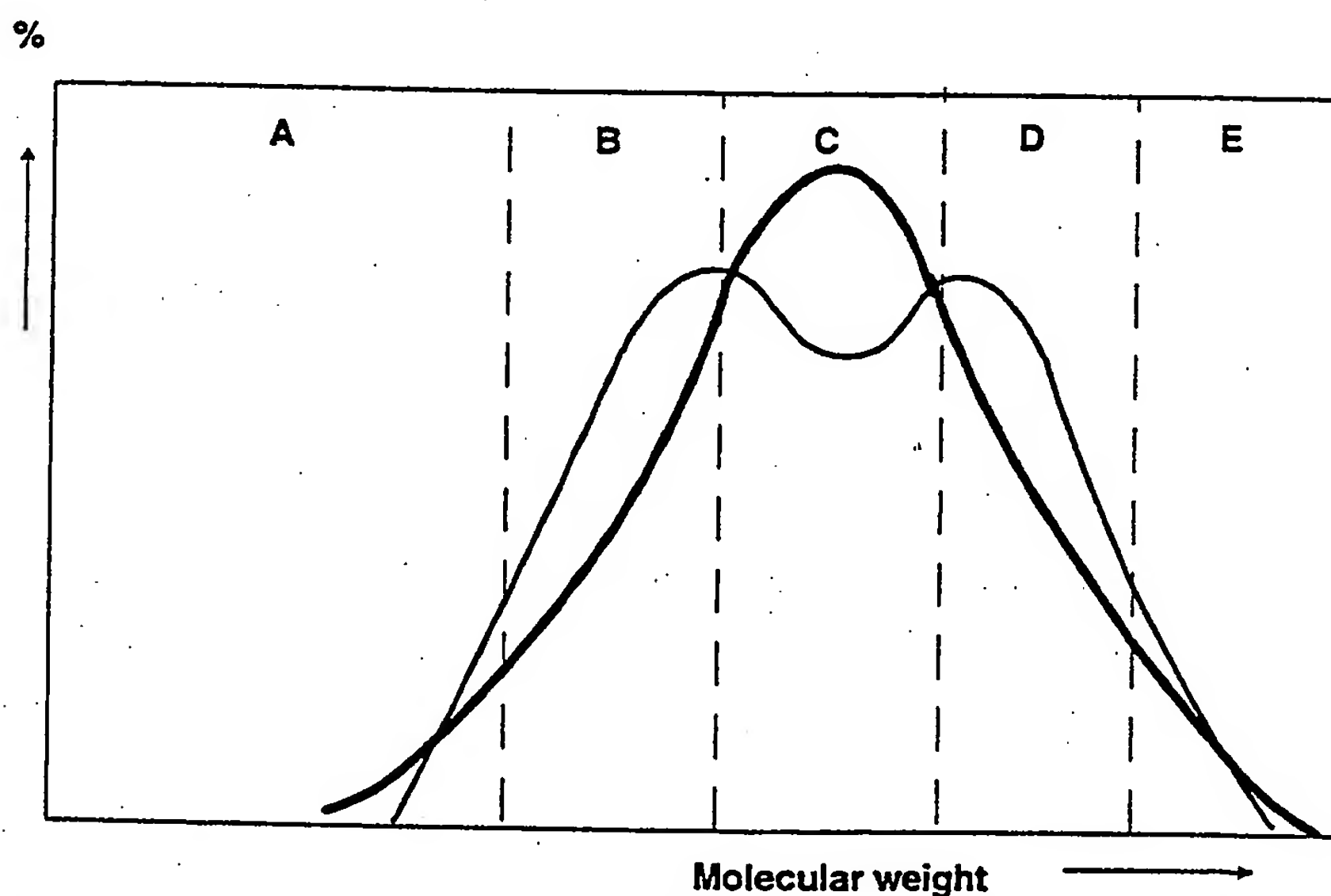
Figure 10. Illustration of a bimodal molecular weight distribution and the affiliation on polymer properties [74].
Bold lne - traditional molecular weight distribution
Hair line - bimodal molecular weight distribution
Sector A - smoke formation and odour in extrusion
Sector B - improved processability and strength
Sector C - bulk
Sector D - improved mechanical properties
Sector E - improved melt strength

In addition to bimodal processed polypropylene, metallocene PP and PP copolymers are establishing new marketing areas for the PP family. The packaging sector constitutes more than one third of the total consumption of polypropylene. The main applications are films and sheets. Random copolymers are being developed to improve transparency and sealing properties of the oriented or non-oriented films. Metallocene grades clearly produce interesting possibilities for homopolymers whose melting and mechanical properties can be changed.

Fibres and the automobile industry further account for one third of consumption, where PP is used in textiles, matrix in reinforced structures, compounds and mineral filled structures. A potential application in the automobile industry would be foamed fittings and dashboards, where new processing technologies could give the required properties to replace crosslinked polyethylene with a recyclable polymer [75].

2.4 PP Film Manufacturing

The most common blown film die design is the spiral mandrel type (Figure 11) It has four main components; the mandrel, the body, the inner lip and the outer lip. The polymer melt flows mainly in the spiral channels, which are grooved in the mandrel. To make the melt uniformly distributed in die gap the flow also occurs partly across the spiral gap (Figure 12). In processing of non-Newtonian fluids with spiral mandrel die, the exit flow consists of several flow, time and temperature histories. Even a single layer film contains invisible stripes caused by different flow gradients in channels (main flow) and in gap (leakage flow). The flow behaviour in spiral mandrel follows the principle, where several flow gradients are produced in capillary and slit dies [3, 33]. The target in the end is to minimise thickness variations to produce a uniform film. The die is often rotated in order to improve film roll geometry when winding large rolls [55].

Generally single and multilayer PE films are produced by blown film technology. Blown film technology is not as suitable for polypropylene or polyester because of their high crystallinity and low melt strength. Rapid film blowing demands high extensional viscosity of the polymer to bear film formation and molecular orientation in the region before the frost line. One of the advantages in using film blowing is the ratio of molecular orientation in

machine and transverse directions, which can easily be controlled and varied during processing. Oriented films can also be produced by blown film technology. The circled extrudate has to be cooled (crystallised) and reheated again for bubble stretching. Crystalline structure is produced in cooling to make spherulite deformation and orientation feasible. Orientation occurs if the temperature in bubble stretching is kept under the melting temperature of a single crystalline. The form of the polymer is rubberlike, which is a result of flexibility of the amorphous region and spherulite deformation under stress.
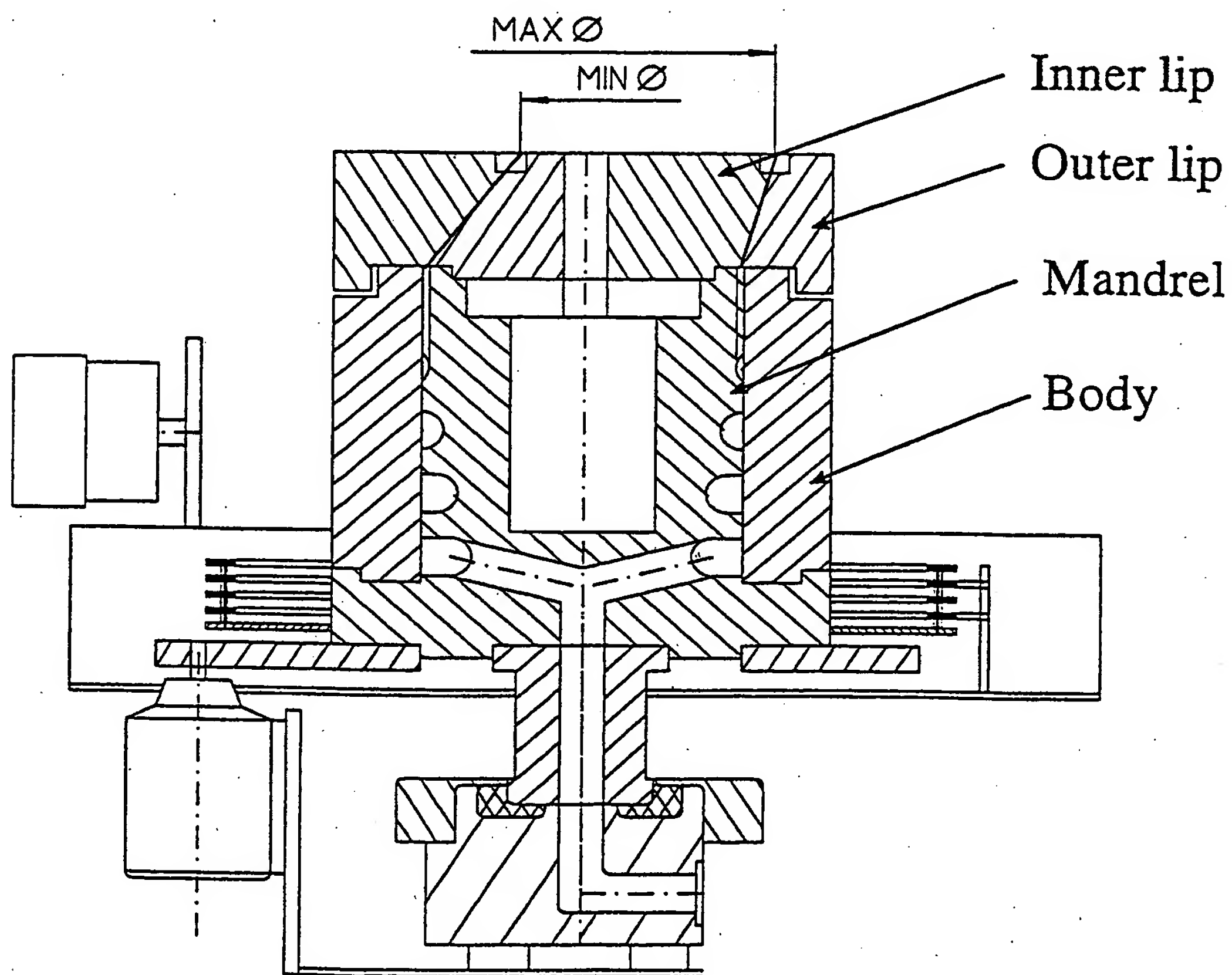
Figure 11. The principle of rotating spiral mandrel die [55].
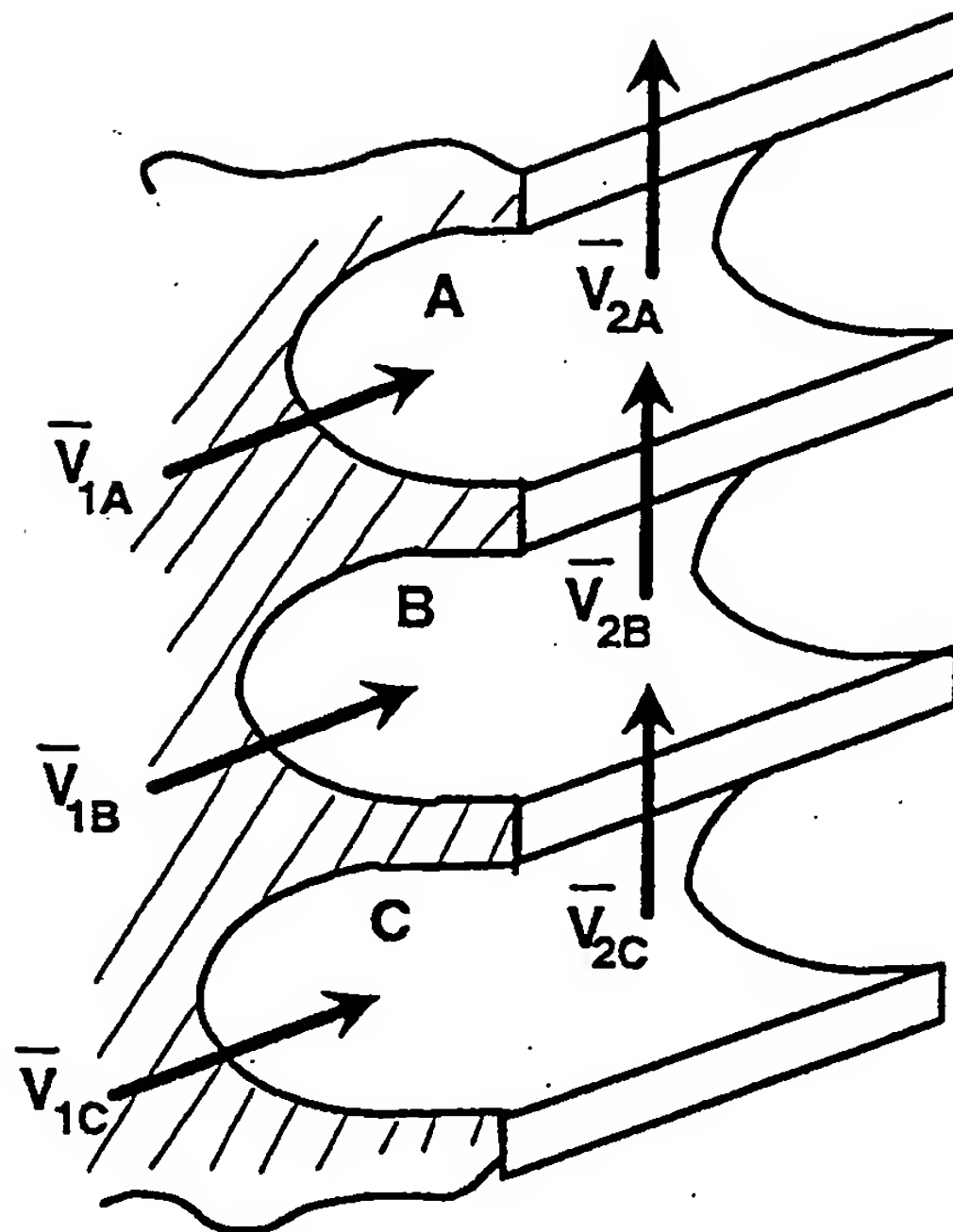
Figure 12. Flow distribution in a spiral mandrel die.

$\overline{V}_{1A}, \overline{V}_{1B}, \overline{V}_{1C}$ = main flow in spiral channel

$\overline{V}_{2A}, \overline{V}_{2B}, \overline{V}_{2C}$ = leakage flow to destroy spiral marks

Non-oriented polypropylene (NOPP) entered the markets immediately after PP was publicised. Oriented polypropylene (OPP) came in the 1960s. Chill roll cast process and tenter frame process are the most popular in the production of NOPP and OPP. Nowadays biaxially oriented polypropylene (BOPP) is the most manufactured film in the PP family. The principle of BOPP blowing film line will be introduced in Chapter 3.3.3.

In chill roll NOPP process polymer is extruded through a flat die on a chill roll with controlled temperature. High melt temperatures and low quenching temperatures favour low haze and high gloss. Molecular orientation occurs mainly in machine direction due to drawing.

In the tenter frame BOPP process polymer melt is extruded on chill roll with water bath as a thick sheet. The sheet is heated again and stretched first in the machine direction and then in transverse direction at a temperature near the

machine direction and then in transverse direction at a temperature near the melting point. The orientation ratio can be controlled up to a certain limit and is more difficult to adjust, especially in transverse direction. The process itself is demanding for polymer because of stretching in two steps and the technology is very expensive. The thickness of the film may be as low as 5 μm and the film is highly transparent. Transparency can be improved because of effective cooling, which can be organised more easily with the help of cooling roll and water bath. Most of the BOPP films today are produced through the tenter frame process (Figure 13).
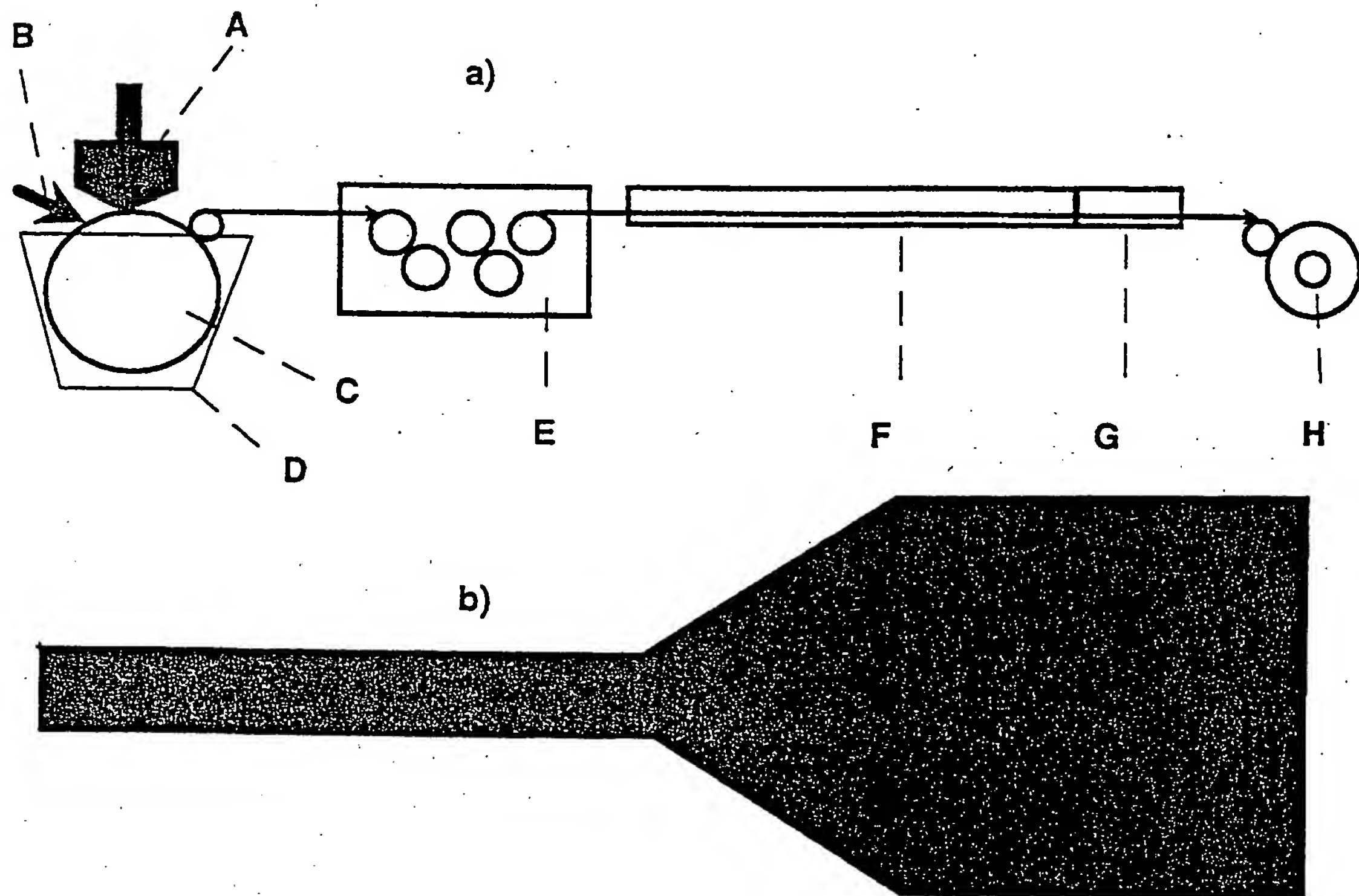

Figure 13. Illustration of a tenter frame BOPP line from side view (a) and film profile (b).

A) Extruder

B) Air cooling

C) Chill roll

D) Cooling bath

E) MD orientation

F) TD Orientation

G) Annealing

H) Winding

There are generally two main targets in BOPP manufacturing: highly transparent and highly opaque films. To reach high transparency, the extrudate has to be cooled quickly to achieve high density but small size of crystallites. Polypropylene can also be modified for high transparent film purposes by adding nucleators or with chain modification (random polymers) as discussed earlier.

High opacity is commonly attained by titanium dioxide. Cavitated films, which has been discussed in Chapter 2.1.5 give an opportunity to increase the opacity to a high extent. High opacity and flexibility under nip pressure improve the printing properties of cavitated films. BOPP films are often metalled or lacquered to increase gloss and barrier properties or to improve heat sealing. Afterwards BOPP films are used in many packaging applications; laminated pouches and wrappings for food, and cold sealed films for chocolate, ice cream and biscuit. They are also widely applied in capacitor films [55].

3. EXPERIMENTAL PROCEDURE, RESULTS AND DISCUSSION

3.1 Background

The innovation of foamed BOPP film started in Tampere University of Technology (TUT) in the 1980´s. The impulse was finally given by United Paper Mills (UPM) to start the pilot production of foamed packaging films. Because of the high sensitivity of the process and partly because of the unpredictable properties of the film, the invention did not so far reach the industrial level. Nevertheless new applications appeared soon to utilise foamed BOPP films in Electro Mechanical Film (EMF) applications, which has been discussed further.

The new rotor die design used in this thesis was unique but the same principle can be noted in dies produced by Brampton Engineering Inc. in USA. They also utilise stacked dies, where the number of layers can be changed by adding a new die plate on top. The invention around three layer rotor die was a kind of prestep into a large extrusion development project started in the Technical Research Centre of Finland (VTT) and which is still continuing.

The experimental part of this study can be divided into three main items:

Foam technology, where equipment has been developed for polypropylene foam extrusion with a capillary die, multilayer blown film die and biaxial orientation.

- Material properties, where the effect of the viscoelastic properties of three different kind of polypropylenes on foaming was studied.
- Processing, where the effect of extrusion parameters on foaming was measured

The idea was to produce highly foamed PP tube and oriented film in extrusion with a foam extent over 50 %. The experimental studies were started from the standpoint of a microcellular foam structure. Standard blown film line served as a base manufacturing line, which had to be subjected to major modifications during the studies.

3.2 PP Foam Extrusion Machinery and Foam Analysis

The right technology as well as special properties of polymer play an important role in foamed polypropylene extrusion as the study will show. In order to expand PP into a fine low density microcellular form, the optimal properties of foamable polypropylene had to be defined together with product allocated technology before a successful result.

Heterogeneous foaming was chosen as a base method and justified as in Chapter 2.1.1., when low density microcellular foam structure was targeted. The blowing agent was environmentally safe nitrogen gas, which was compressed straight into the extruder. A small amount of chemical foam nucleating agent was added in polypropylene matrix to produce foam embryos before final expansion. The effect of processing conditions and foaming nucleators on the final foam structure was studied and rheological properties were measured with a cone and plate rheometer and slit die extrusion.

Polypropylene was chosen as a base material because of its potential as a packaging film and sheet at high temperature applications compared to PS and PE and also because of its high orientability.

3.2.1 Extruders

Two (DOLCI 45 T) extruders constituted the base machinery for the studies. The diameter of the screws was 45 mm. Skin extruder (screw length 20 D) formed solid layers on both sides of the foamed middle layer extruded by foam extruder (screw length 25 D). Thin surface layers encapsulate and stabilise the foam structure and make a smooth surface on the final product and finally the foam extent and processing can be promoted. Screw dimensions are introduced in Figure 15.

Chemical foam nucleators, particle nucleators, surface active agents and blowing gas is commonly needed in polymer foam extrusion. All the components should be effectively and homogeneously mixed with plastiziced polymer [7]. For this purpose the foam extruder was equipped with both CTM and UC mixers (Figure 14).
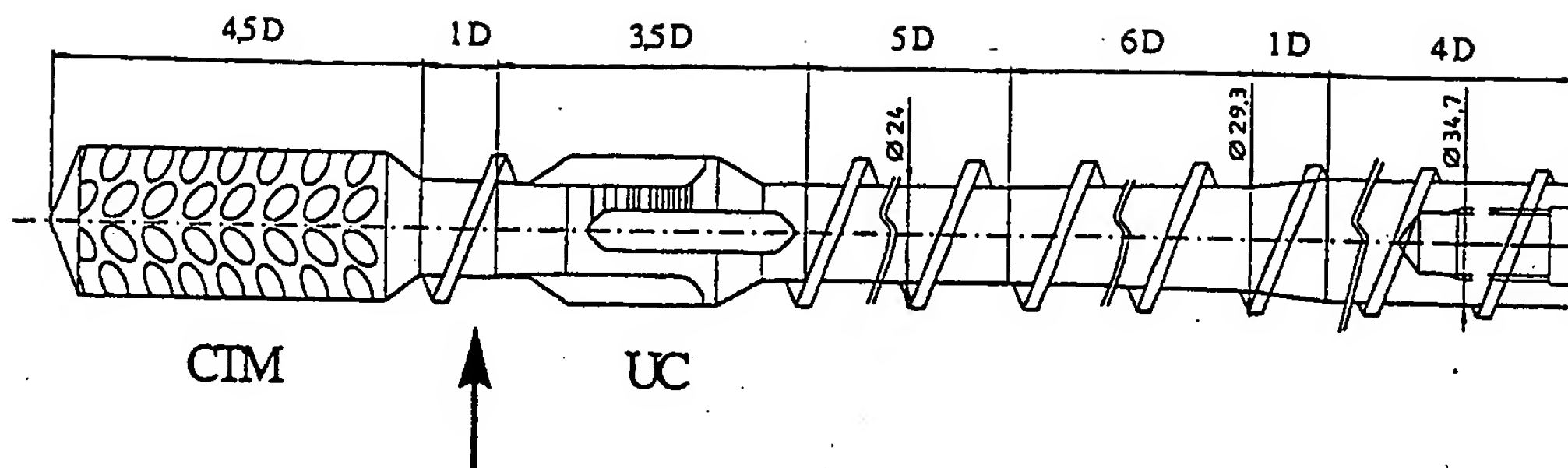
Figure 14. Dimensions of the screw used in the foam extruder;
CTM = Cavity Transfer Mixer
UC   = Union Carbide Mixer, Maddock Mixer
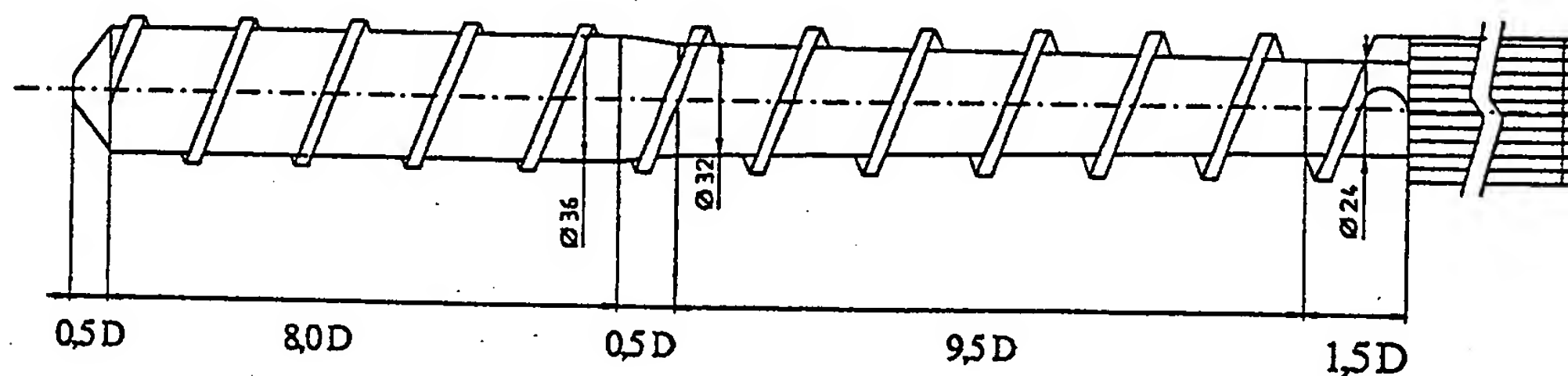*The arrow indicates the inlet of nitrogen.*

Figure 15. Dimensions of the screw used in the skin extruder.

Nitrogen gas was compressed into the extruder just before the CTM mixer. The site of the gas inlet had to be sought experimentally. If the location of the gas inlet was too close to the plastizising zone of the screw, gas started to flow backwards to the hopper, and extrusion became impossible to control. The gas inlet was placed between the screw mixing gap, where the polymer was well plastiziced and back pressure sufficiently high. There was no significant difference if the gas inlet was placed before the UC mixer and presumably the time in extrusion criterion does not play a major role increasing solubility of the blowing agent.

The flow of the gas into the extruder started straight after the pressure of the gas reached the pressure of the polymer in the cylinder. The saturation pressure was reached fast when the gas pressure was increased. If the pressure was further increased, the extra insoluble gas flowed away separately from polymer causing small explosions in the die exit.

Gas was compressed through the diamond hole with a diameter of 10 microns. The smaller the gas inlet the better the amount of gas and saturation pressure could be defined.

3.2.2 Dies

A capillary die (Figure 16) was used to measure the effect of process parameters and additives into the foam structure. The die hole diameter was 0.8 mm, which was fixed so that the pressure in the extruder was the same as it was in test runs with the three layer die. The capillary die produced a pressure about 100 bars at the screw end.
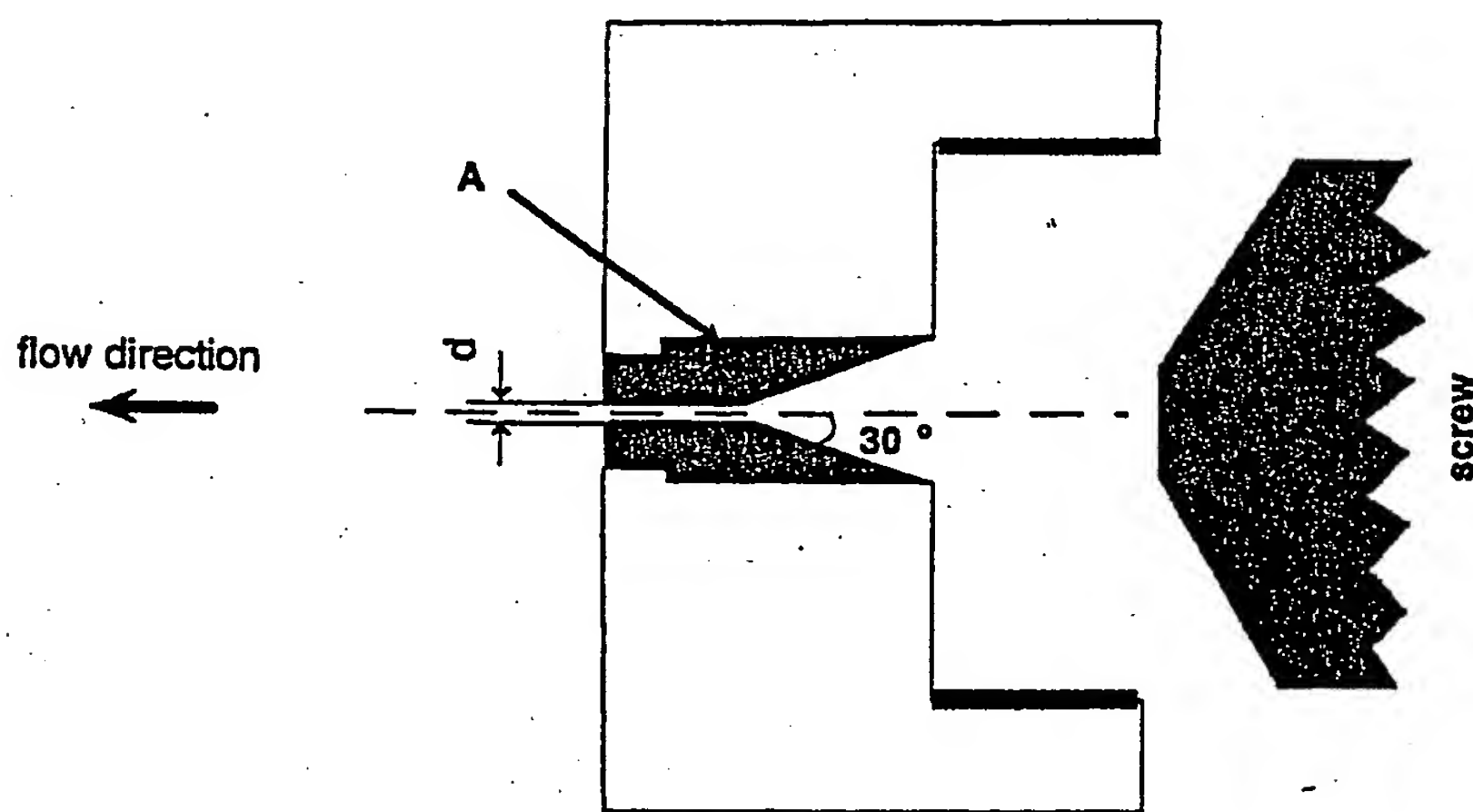
Figure 16. Capillary die for foam evaluation.
d = capillary diameter
A = replaceable die core

The experimental foam extrusion studies for more commercially interesting fields, films and pipes were done with the spiral mandrel die at the beginning of the work. However the leakage flow of spiral channels was insufficient to destroy the marks of the channels. Solid films could easily be blown, but material foaming revealed the flow memory of viscoelastic material as stripes immediately after die exit. Flow in spiral channels and leakage flow form bubble embryos concentrates, which can be seen as solid stripes and joints of extrudate. Foaming highlighted the different flow history in visible foam stripes, which means the flow, time and thermal history have to be mixed more effectively in order to get a uniform extrudate. It was concluded that a new die design had to be developed.

A new three layer die geometry was developed especially for foaming applications. The basic aim of the die was to destroy the flow memory of the extruded polymer melt as thoroughly as possible. The "dead" corners were eliminated and residence time through the die was equalised by making the flow channels like tentacles into the middle of the mixing device. The flow distance was always the same from the incoming of the polymer in the die into the circle of the mixing rotors (Figure 17).
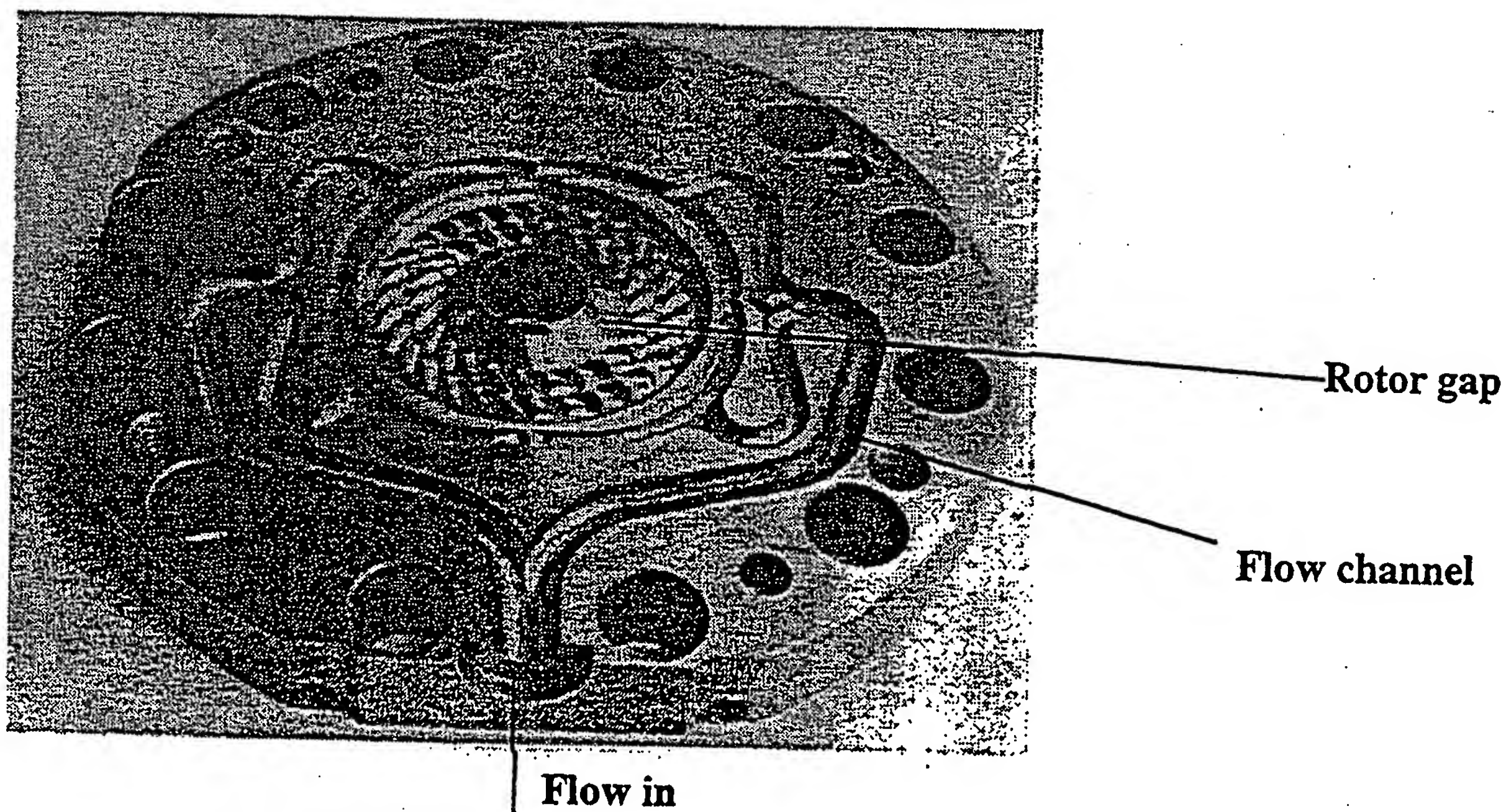

Figure 17. Flow channels in the stator of the freely floating model.

The die was set up from four steel plates, all of the same shape as described in the previous section. The first idea was to use freely floating rotors between the plates, where the acting force was assumed to be the flow rate and pressure gradient inside the die (Figure 18). This was unfortunately insufficient; both flow rate and pressure gradient were too low and ineffective. The problem was solved by externally rotated rotors (Figure 19). The final mixing appears in the middle of the die where two cogged rotors, whose speed can be adjusted, destroy the flowing memory of the polymer. The rotors float between two die plates, stators, whose surface is also cogged. Rotor-stator gap ensures effective mixing. Plasticized and mixed polymer melt is then pushed towards the die exit where the different layers joined on the die mandrel (Figure 20).
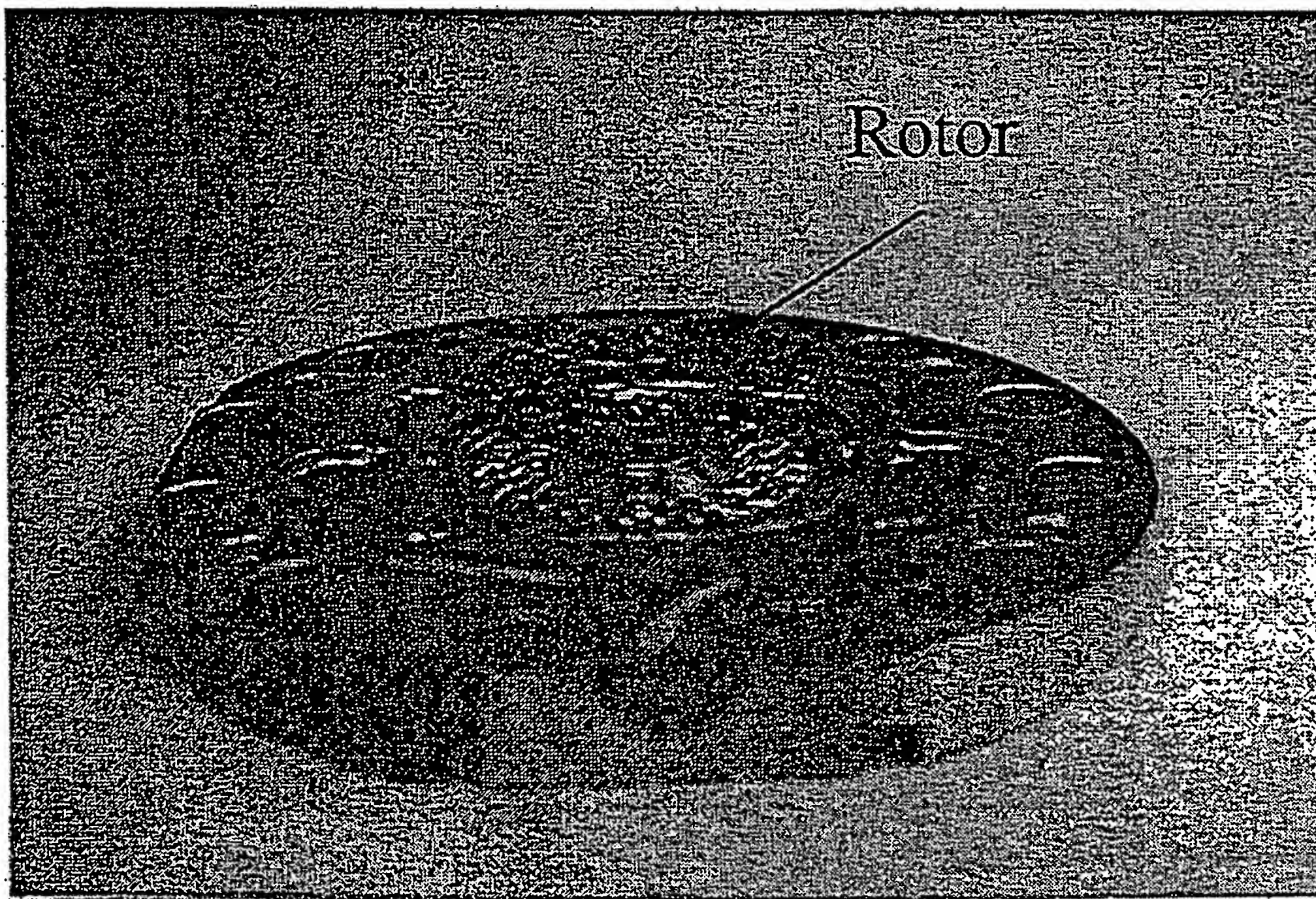
Figure 18. Freely floating mixing device of one layer plate in three layer die.
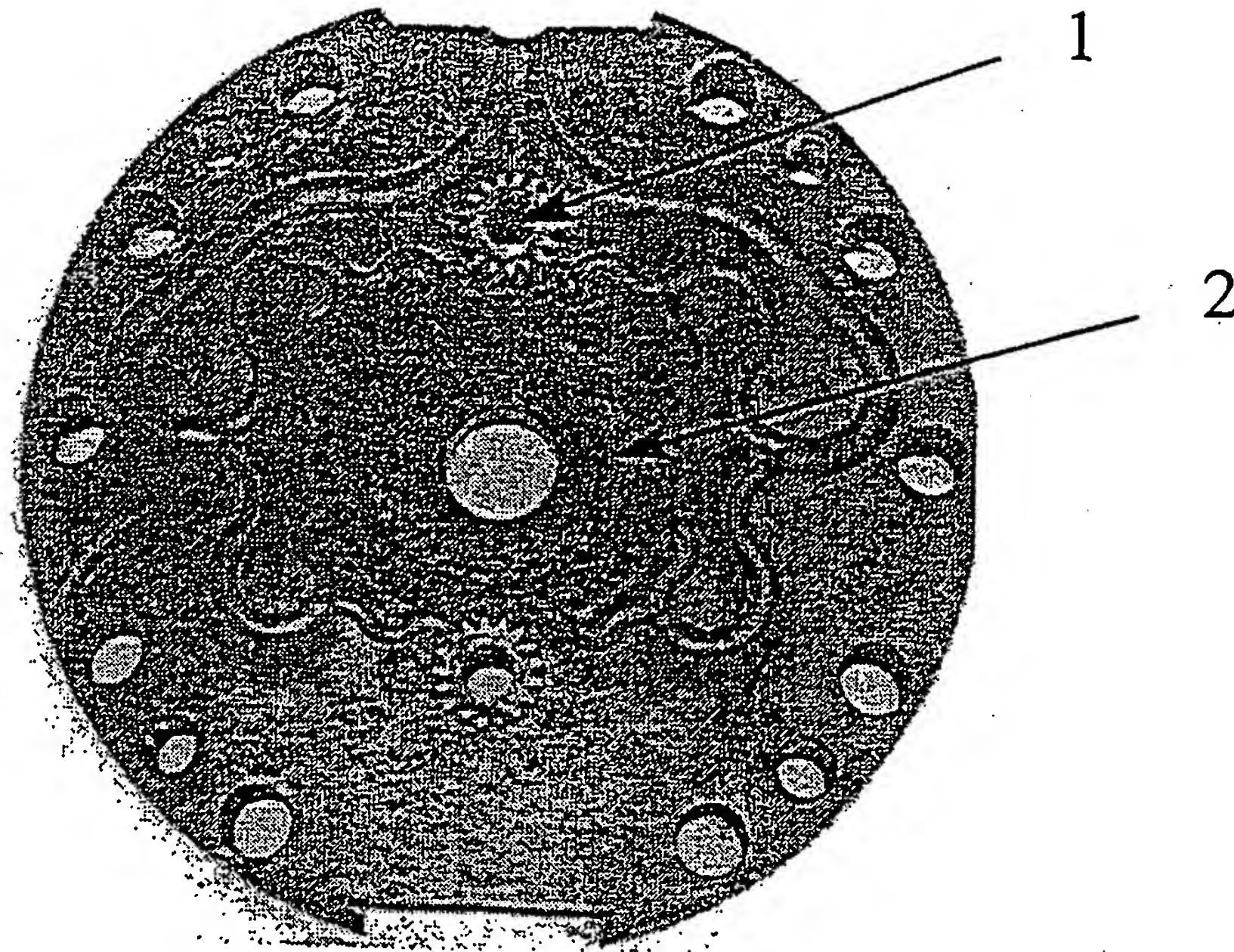
Figure 19. Externally rotated mixing device of one layer plate in three layer die [39].

1 = rotating cog

2 = rotor

Wall thickness profile of the extrudate was controlled with a floating mandrel which could be bend at a low angle to change the flow distribution between the mandrels. Inner torpedo was also bendable from the attachment on the bottom surface of the die. Thickness variations of the tube were in limits of 10 % and in the BOPP film 20 %. Even though the thickness profile was quite large the pilot line served the studies in extrusion foaming well, and enabled a technology for oriented film production. Today thickness variations in blown film technology is more or less under control with an air ring in bubble blowing whose air temperature is controllable. Air ring can be connected in line film thickness gauge control, which can further be associated in die lip control [55].
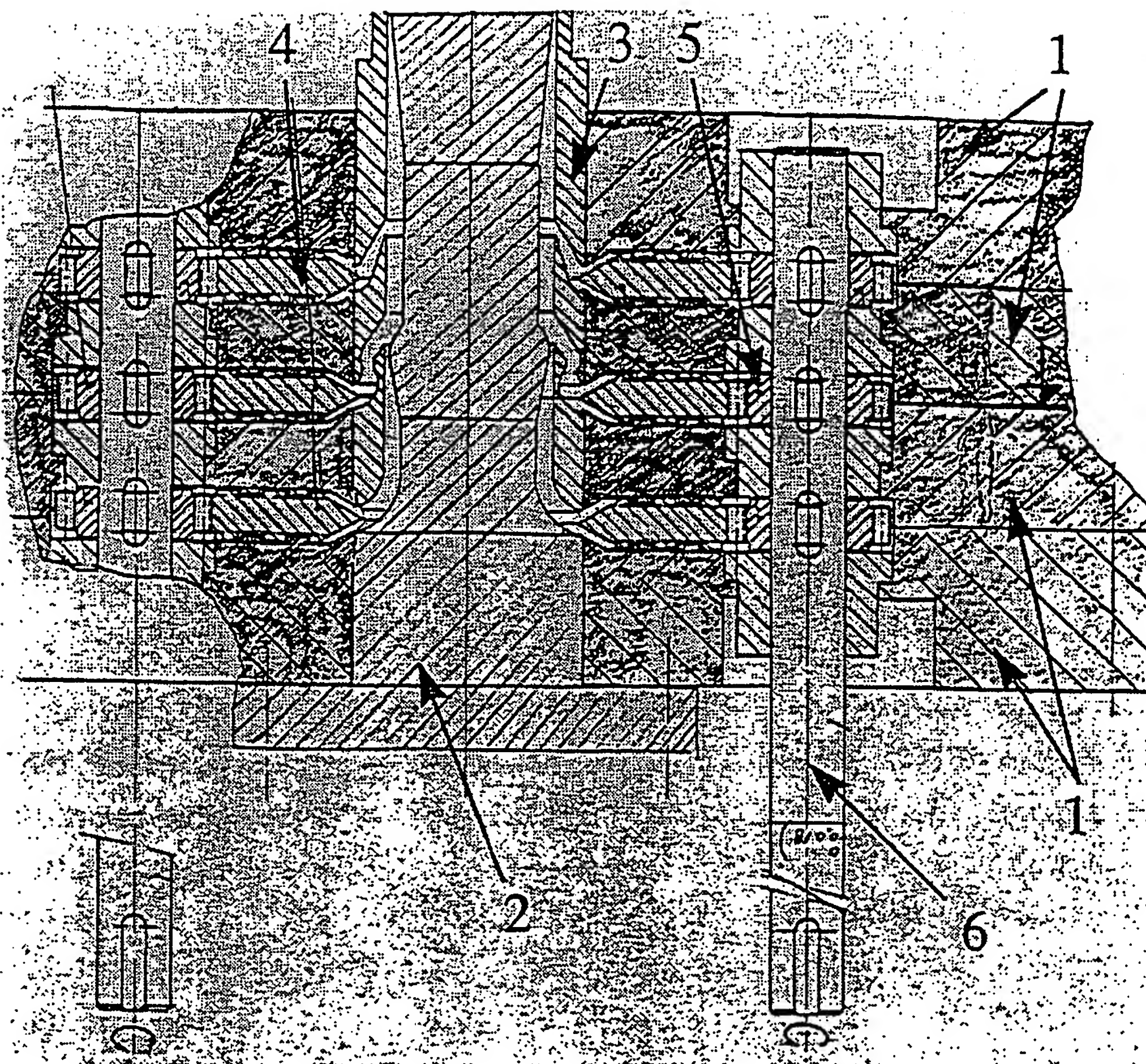
Figure 20. Three layer foam extrusion die with externally rotating rotors [39].
1 = Die plates
2 = Inner torpedo
3 = Floating mandrel
4 = Rotor
5 = Cog
6 = Rotating axle

The structure of the die was developed so that it can easily be modified into 5, 6, 7,... layer die by only making a new plate on top. Therefore it gives the possibility for barrier multilayer foam structures and applications. The level of inner torpedo and floating mandrel had to be kept close to equal. Otherwise the flow in the die exit was disturbed because of rapid expansion (bubble growth) of the extrudate. The expansion of the polymer could be compared with maximised

the extrudate. The expansion of the polymer could be compared with maximised die swell effect, where viscoelastic material swells after a heavy load in extrusion. Therefore equal level of mandrels ensures symmetrical swell in die exit.

The torpedo temperature affected on the final foam result decisively. If the temperature deviation between torpedo and polymer melt was more than 5° C, the polymer flow was disturbed and it caused a pumping effect in the die exit area. This is the reason why the torpedo was drilled for thermocouples from the bottom. The result can be explained through different flow velocity profiles on channel walls which is in consistent with the studies by Han [3].

3.2.3 Biaxially Oriented Foam Film Line

Figure 21 introduces the foam stabilisation in die exit, where the polymer expands immediately after the external pressure drops. The foam structure is stabilised on the cooling mandrel and encapsulated with thin solid layers to produce a smooth surface and uniform foam quality (Figure 22).

The cooling mandrel had to be engraved (Figure 23), because the foaming gas of the middle layer was slowly penetrating between the mandrel and PP tube causing small ruptures in long term runs. The blown film easily burst from interrupted regions. By engraving small spiral channels into the mandrel, the penetrated gas was led away from the mandrel surface. The interruptions were eliminated and film blowing became feasible. Thicker skin layers also retarded the diffusion of blowing agent.
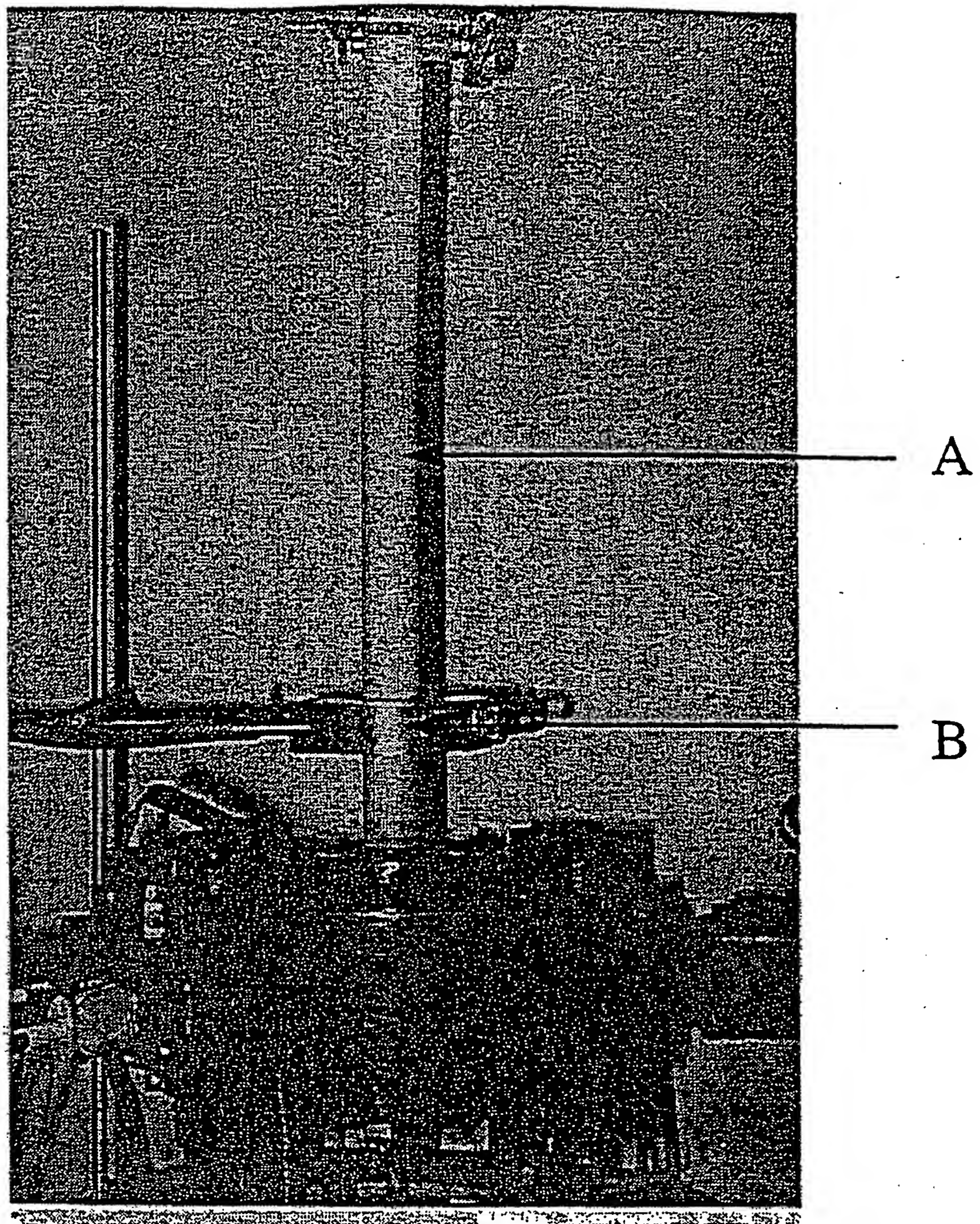
Figure 21. Externally air cooled and internally mandrel chilled foam tube.
A = Foamed PP tube (Cooling mandrel inside)
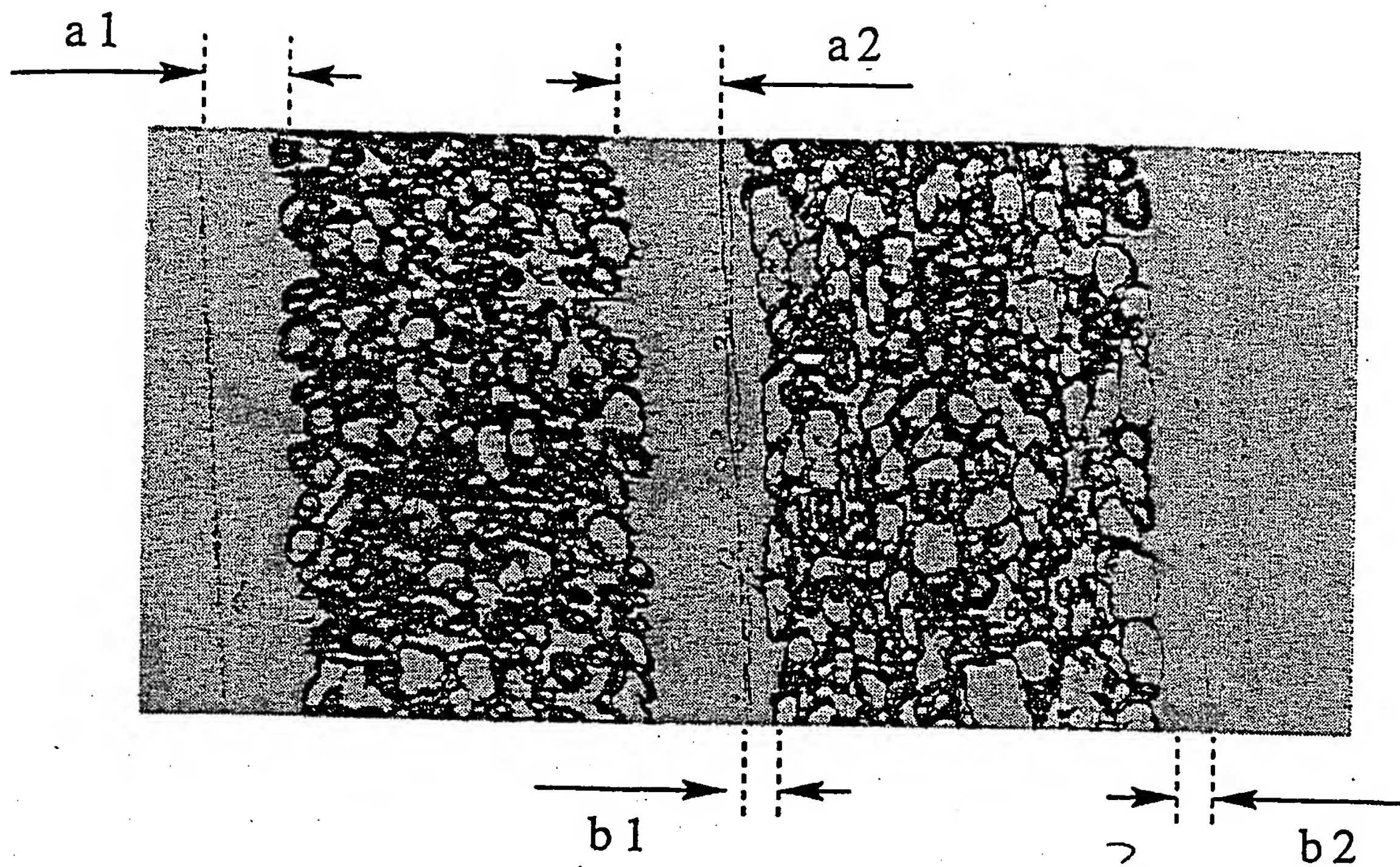*B = Air cooling ring*

Figure 22. Cross section of foamed tube. 100X.
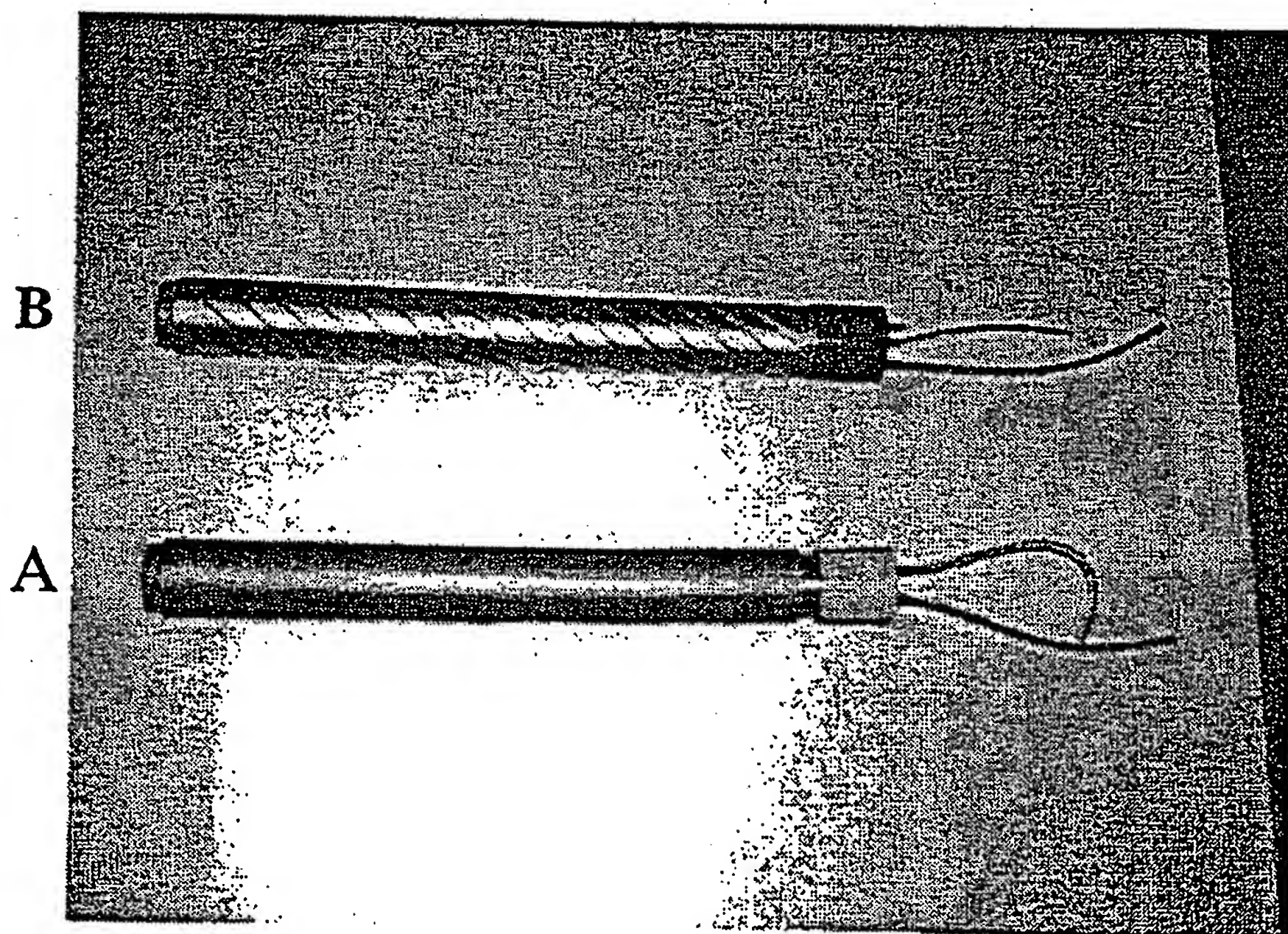a1, a2 = thick skin layer
b1, b2 = thin skin layer

Figure 23. Water cooled mandrels for A) solid and B) foamed extrudate tube chilling.

Cooling mandrel was anodised aluminium, making the surface hard and smooth for tube to slip on. Teflon or silicon was sprayed on mandrel lowering the friction temporarily to help the drawup. The shape and the diameter was fixed according to the shrinkage of foamed polypropylene. It was obvious if the mandrel was too tight, the forces of friction easily caused sticking of the extrudate. If too loose, the film blowing pressure might flow from the top of the mandrel down to the section, where polymer was still fluid and burst the soft tube. The mandrel was shaped to adapt the cooling and coexistent shrinking of the polymer. The diameter of the mandrel was larger immediately at die lip to decrease steadily into a "hat". The hat was like a final plug on top to keep the film blowing air above. The hat was slightly conical increasing in diameter upwards and causing high friction. The teflon hat as a low friction material was a reasoned choice in this case. The temperature of the mandrel was from 5 - 10 °C. Higher temperature delays cooling and causes difficulties in film blowing. Water flow was channelled to give highest efficiency in the bottom of the mandrel to warm upwards by conduction.

Figure 24 introduces the pilot line equipment, where the cooled tube was first reheated in the oven up to 140 °C for orientation. The inside pressure in the tube blew it into a thin film just on the upper infra-red (IR) heaters, when the tube was softened becoming rubberlike. If the temperature was too high, the elongation strength was rapidly lost causing the film to burst. Because of simultaneous stretching in machine direction (MD) and transverse direction (TD), the film was oriented biaxially. Finally an air ring cooled the film and it was connected between teflon frames to be pressed into the upper nip and reeled.
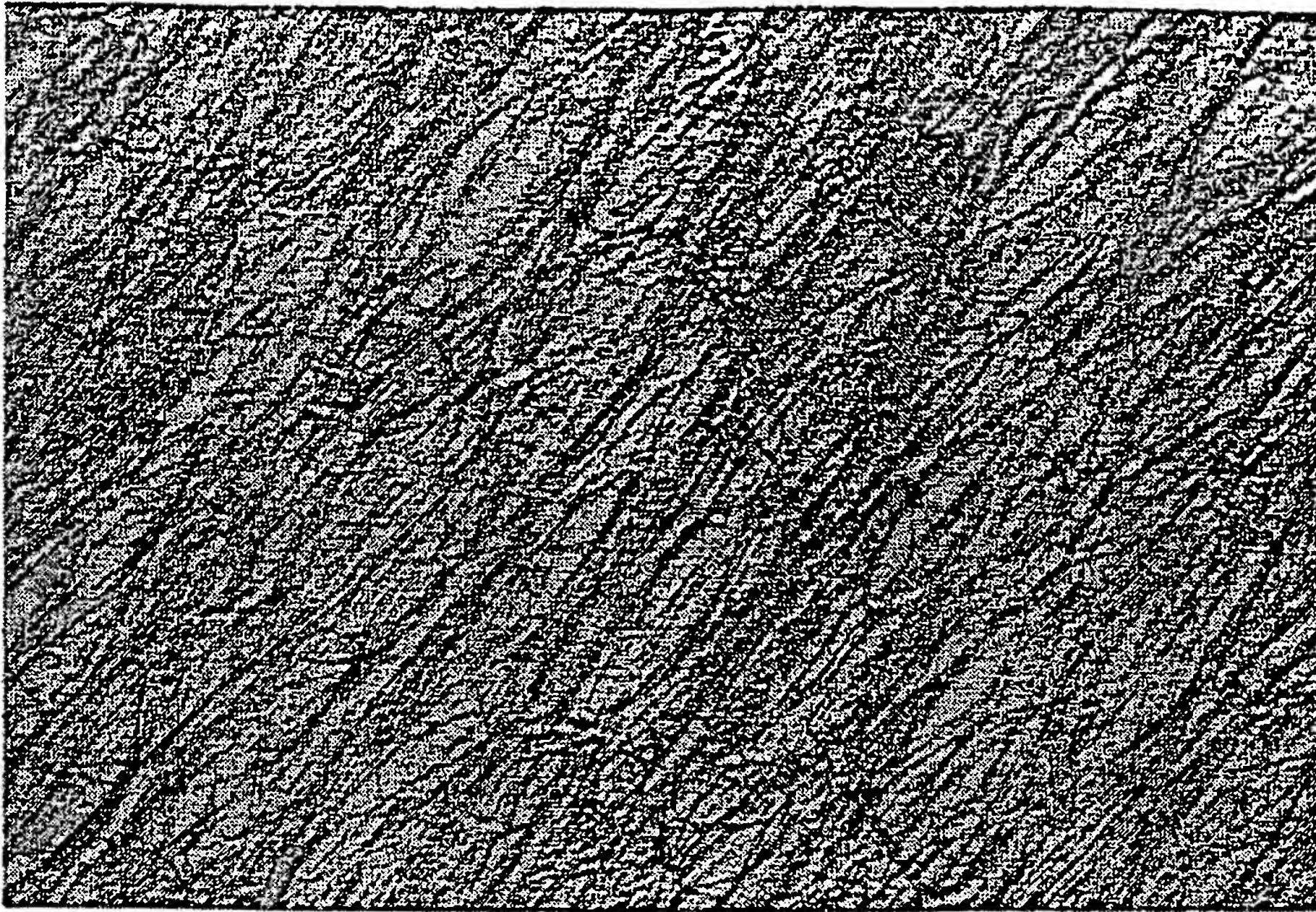
Figure 24. BOPP foam film line.

The BOPP foam film was full of lenslike cells whose walls are very thin (Figure 25). Many foam cells on top of each other also means many thin interfaces inside the film, making the film opaque. The smaller the foam cells are, the higher opacity can be achieved.

Figure 25. Lenslike cells in biaxially oriented foam film (100 x).

The walls of the cells were stretched thin already in the die exit foaming and the extensional viscosity was already near the critical point of break before orientation, because the tube without skin layers was broken even in low stretching ratios either in tube reeling or at latest in film blowing orientation. The solid layers on both sides could strain in stretching and they keept the structure capsuled, which is consistent with literature of solid skins and sandwich structures [48].

3.2.4 Processing Conditions

According to the theoretical part foam extrusion is strongly dependent on stability and control of process parameters such as temperature, pressure and shear effects. Many times even a slight change in conditions can make the extrudate unsatisfactory, which may be related to melt strength properties of polymers and foaming nucleating agent/foaming agent effects.

The process parameters which were measured and adjusted are collected and presented in Figure 26.
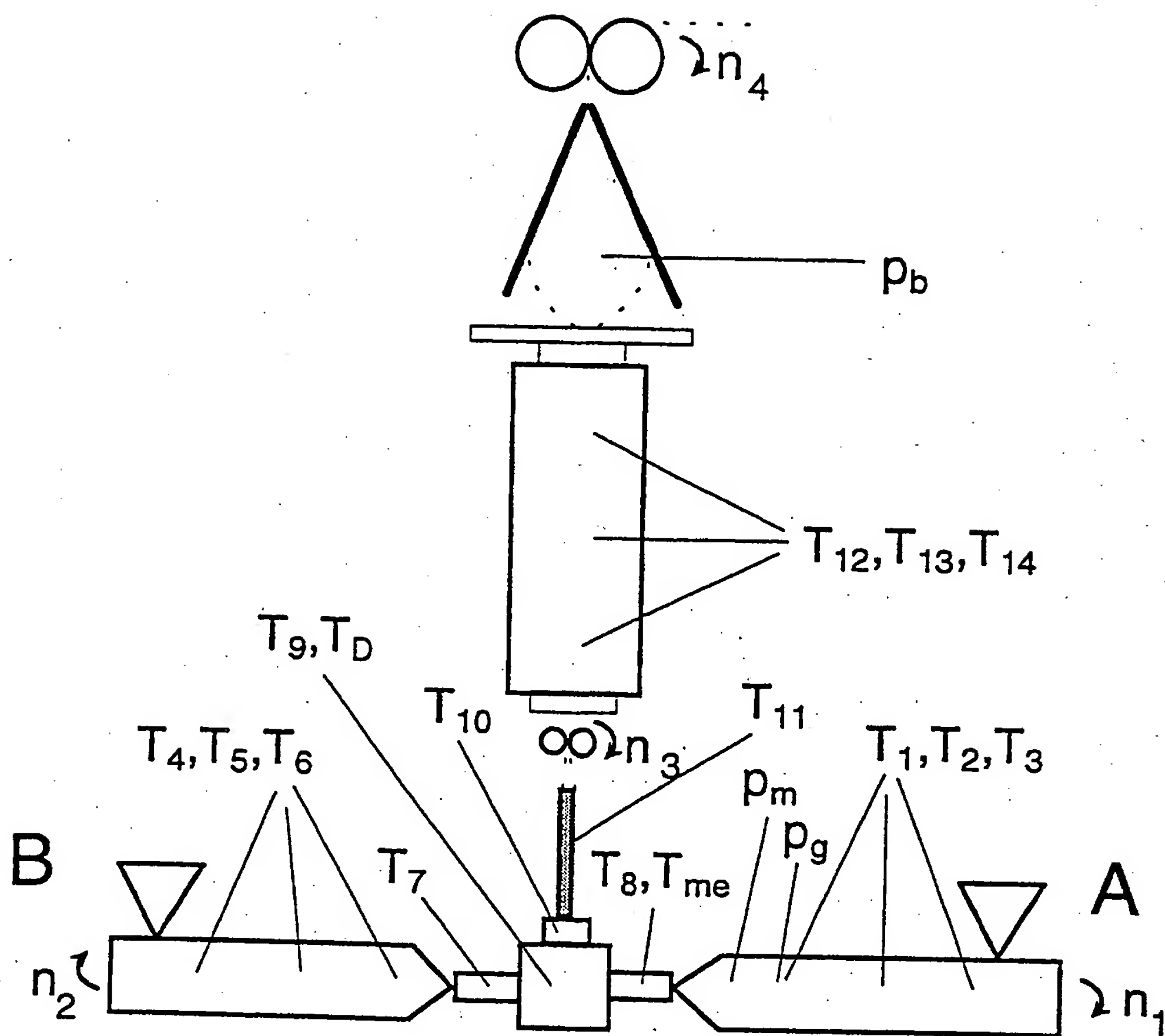
Figure 26. Process control parameters in BOPP foam film line, where
$T_1, T_2, T_3, T_4, T_5, T_6$ = zone temperatures in extruders
T_{me} = polymer temperature in adapter
T_7, T_8 = adapter temperature
T_9 = torpedo temperature
T_{10} = die lip temperature
T_D = die temperature
T_{11} = cooling mandrel temperature
T_{12}, T_{13}, T_{14} = oven temperatures
p_m = polymer melt pressure
p_g = gas compression pressure
p_b = film blowing pressure, film TD orientation
n_1, n_2 = screw speeds
n_3 = tube reeling
n_4 = nip roll speed, film MD orientation
A = foam extruder
B = skin layer extruder

3.2.5 Analyses

The estimation of foam quality was first examined visually and with loop during the extrusion. The most remarkable things to be noted to were cell diameter, shape and foam uniformity. The enlarged evaluation was made with a microscope and foam extent device.

Foam extent and polymer density were defined with a simple method, where a piece of foamed sample was first weighed dry, after which the buoyant force was measured by submerging the sample (Figure 27).
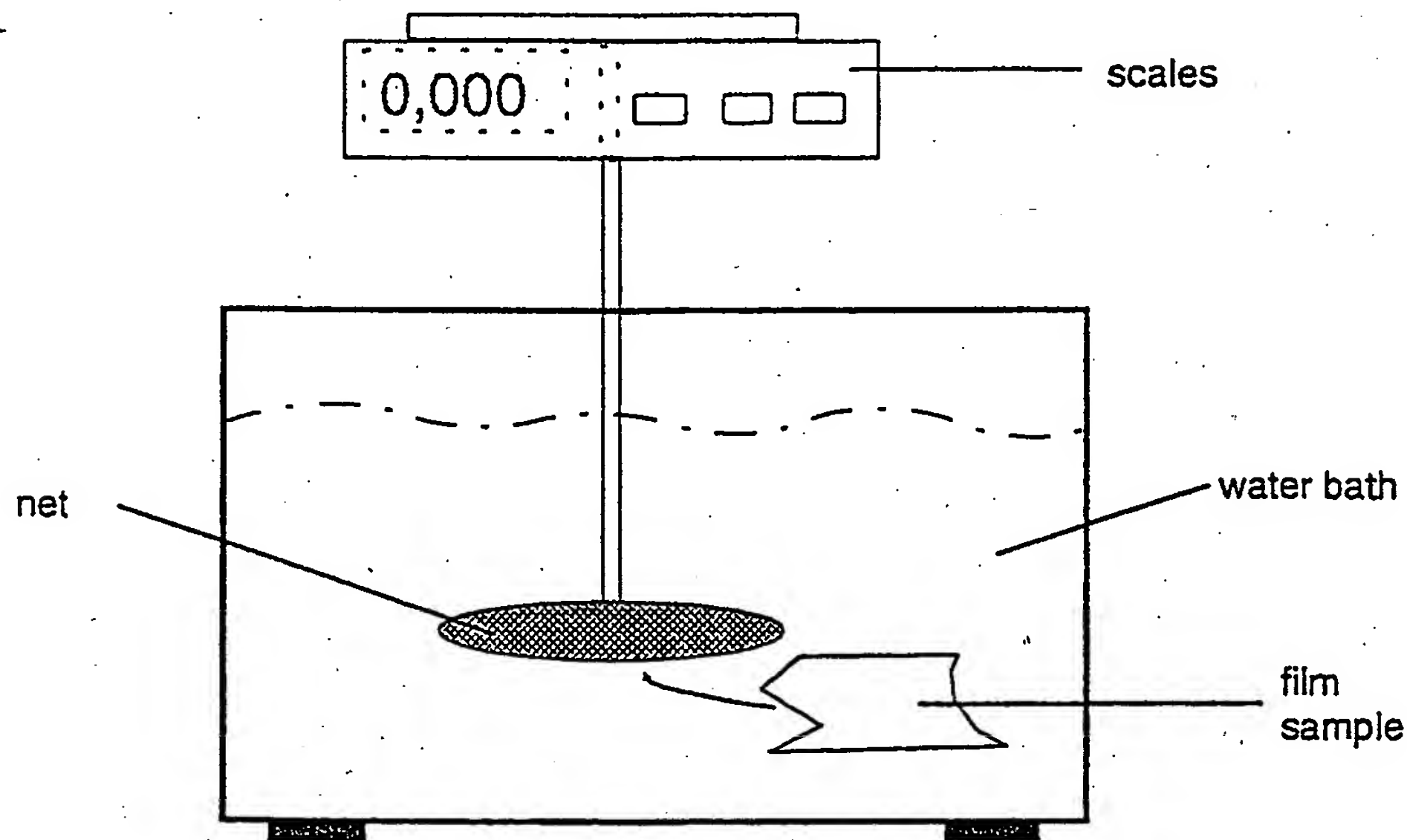
Figure 27. The principle to measure foam extent.

The buoyant force (F_b) was affected in the sample:

$$F_b = mg - m_w g \text{ , where} \tag{12}$$

m   = dry sample weight

g   = 9,81 m/s^2

m_w = weight of the amount of water the sample displaces

According to (12), the density of the sample ρ_s

$$\rho_s = (m\rho_w)/(m - m_b), \text{ where} \tag{13}$$

ρ_w = density of the water

m_b = measured weight affected by buoyant force

A rough, but practical estimation to measure foam extent was made during test runs on the machine, by letting a short piece of foamed tube or string sink freely in a water tub in vertical position noting the wetted length of the sample. If the wetted length was, for example 30 %, a foam extent should be slightly less than 70 %. As is well known the density of isotactic polypropylene ($\approx$ 0,9 g/cm^3) is slightly less than that of water.

3.3 Material Definitions

As has been presented in the theoretical section of the study, viscosity and melt elasticity play an important role in foaming, where the polymer is stretched rapidly into a thin film to produce a foam cell. Polypropylene material developers are therefore forced to search for means to modify the properties, because of the demands of wide applications of foamed products, the economical trend of production of thin films and savings in material costs for oriented and multilayer films. Many times high crystallinity and high melt strength with an easy polymerisation technology is no doubt a challenging aim. It should also be noted that separate technologies and applications demand their own special properties, but when film manufacturing and foaming are considered, many similarities can be found.

The selection of polypropylenes was governed by the extrusion blown film process. All the polypropylenes were commercial grades. HomoPP was a kind of standard blown film grade made by a slurry process (homopolypropylene). CopoPP was a copolymer grade and BimoPP was a high melt strength grade produced by a bimodal process. Molecular structure, thermal and rheological properties were measured to find out the differences in polypropylenes and to help the analysis in foaming.

3.3.1 Molecular Structure and Thermal Properties

As presented in Table 1, crystallinity of copolymer is lower than with homopolymers, as expected. Also, the molecular weight is higher, which leads to higher viscosity. The viscosities are of the level used for PP film blowing manufacturing in general.

Table 1. Thermal properties, crystallinity and molecular weight of polypropylenes.

	HomoPP	BimoPP	CopoPP
MFR 2.16/230°C (g / 10 min)	4.13	2.60	1.65
Homo-/copolymer	Homo	Homo	Co
T_m (°C)	162.8	159.6	163.7
Cryst. %	47.2	46.2	42.5
T_{cr} (°C)	107.9	127.3	114.1
$\overline{M}_n$	57 650	61 500	95 850
$\overline{M}_w$	391 000	414 000	508 000
MWD = $\overline{M}_w / \overline{M}_n$	6.8	6.7	5.3

The graphical illustration in Figure 28 indicates high molecular weight tail in BimoPP, which is typical in polymers produced by bimodal process and supports the theories introduced before. Polymer has higher fraction of high molecular weight constituent. The fraction is set low to avoid dramatic increase in viscosity and uncontrolled flow during processing.
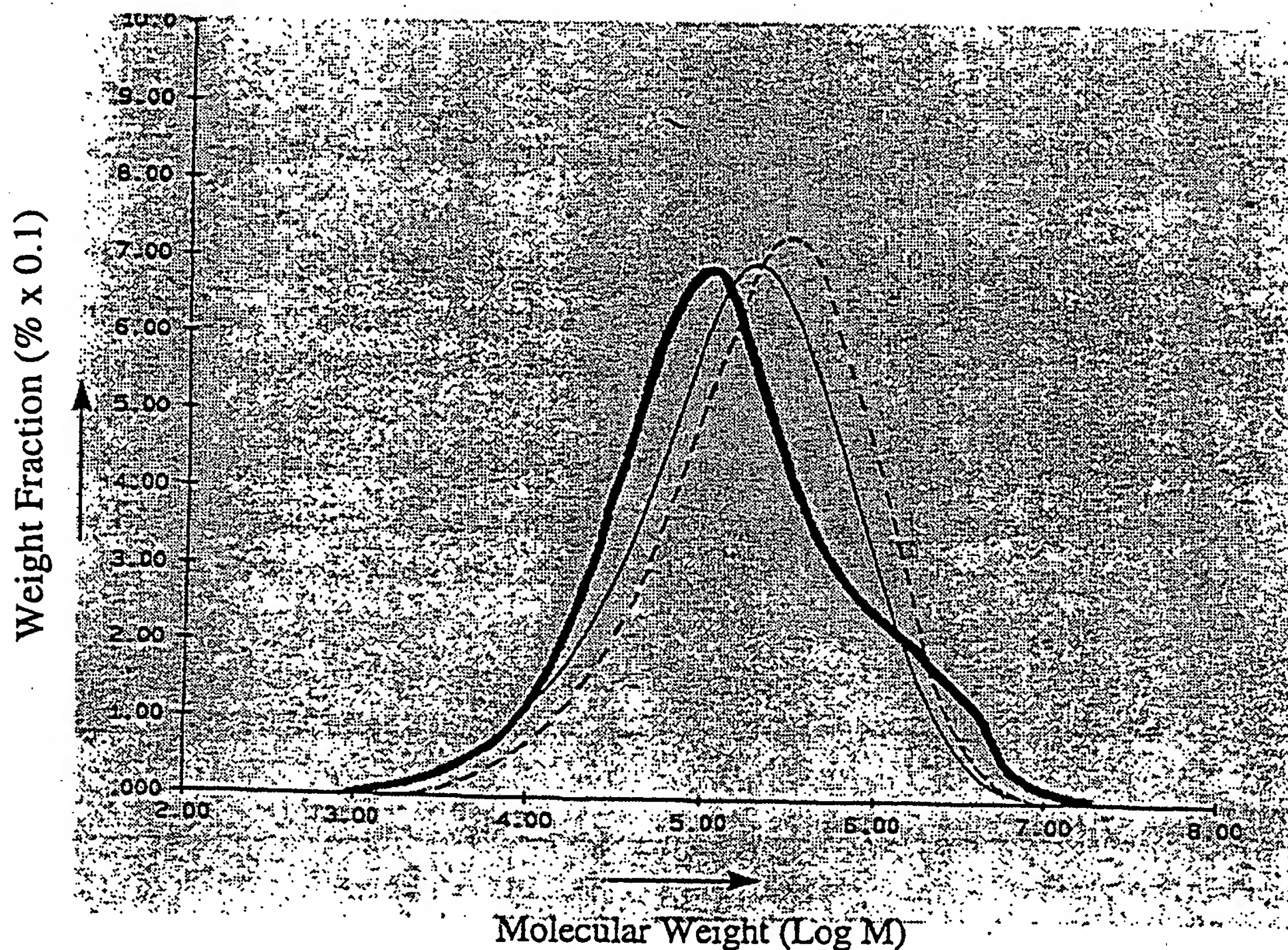

Figure 28. Molecular weight distribution of HomoPP (hair line), BimoPP (bold line) and CopoPP (dotted line).

3.3.2 Rheological Properties with Cone and Plate Rheometer

To increase the understanding of viscoelastic characteristics, whose importance is substantial in extrusion and foaming technologies, it is essential to determine polymer properties in molten state. The Rheometrics RDA-II QC in dynamic shearing mode was used at temperatures of 200 °C, 210 °C and 220 C in nitrogen atmosphere for measuring the rheological properties. A rheometer with

cone and plate tooling with 25 mm diameter and 0.1 rad angle was used. Each test was carried out under the linear viscoelasticity (stress is proportional to strain at a given time and the linear superposition principle holds [76]).

As Table 2 and Figure 29 indicate, the rheological behaviour of BimoPP is totally different compared to other PP qualities. Elasticity values are high, which is consistent with the studies of the high molecular weight shoulder, which increases the entanglement and melt strength properties as described in Chapters 2.1.6 and 2.1.7. High elasticity of polypropylene also consolidates the bimodal polymerisation method of polypropylene.

Table 2. Elastic modulus (G´) and polydispersity (PI) index of polypropylenes at 200°C with cone and plate rheometer. (PI = $\overline{M}_z / \overline{M}_n$, where $\overline{M}_z$ and $\overline{M}_n$ are respectively z- and n-average molecular weight)

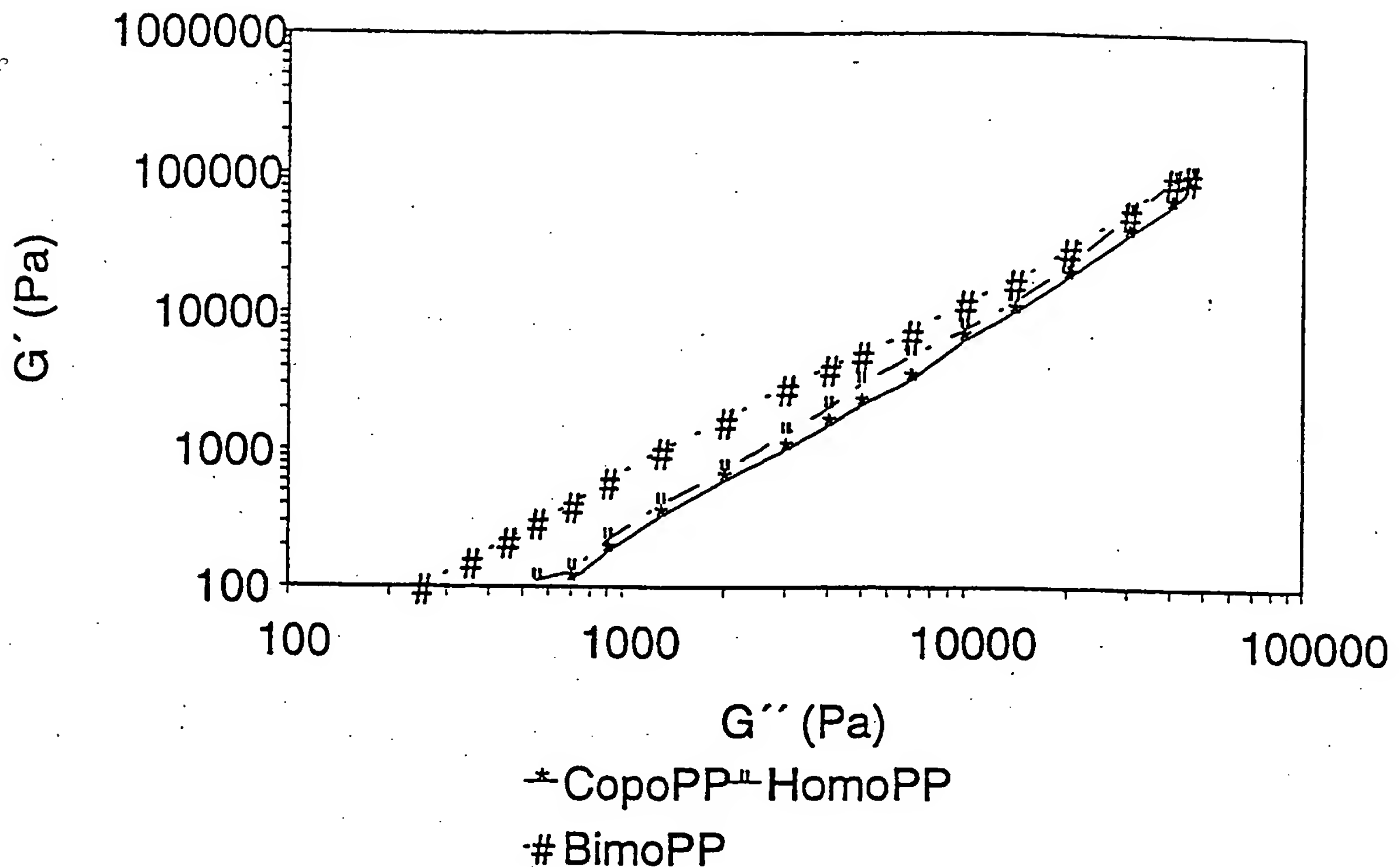|	HomoPP	BimoPP	CopoPP
G´(G´´=2000Pa)	710	1520	550
G´(G´´=5000Pa)	2580	4510	2020
PI	4.9	11.0	3.2

Figure 29. Elastic and loss modulus of the polypropylenes studied at 200°C.

3.3.3 Rheological Properties with an Extrusion Rheometer

To increase the knowledge of rheological behaviour and the effect of rheological properties on foaming in an extruder, rheological measurements were also done with a slit die extruder.

A Muller extruder was equipped with a PE screw and UC mixer. Screw parameters were

$\quad$ D $\quad$ = $\quad$ 30 mm

$\quad$ L/D = $\quad$ 25

A slit die with four DYNISCO TPT 463 E pressure transducers was used (Figure 30). Pressure could be measured from slit die locations P1, P2, P3 and P4. Heating temperature was adjusted with the help of thermal transducers in T1 and T4 to stabilise melt temperature. Measurements were taken at temperatures 210°, 230° and 250 °C and at screw speeds of 20, 30, 40, 50 and 60 rpm.
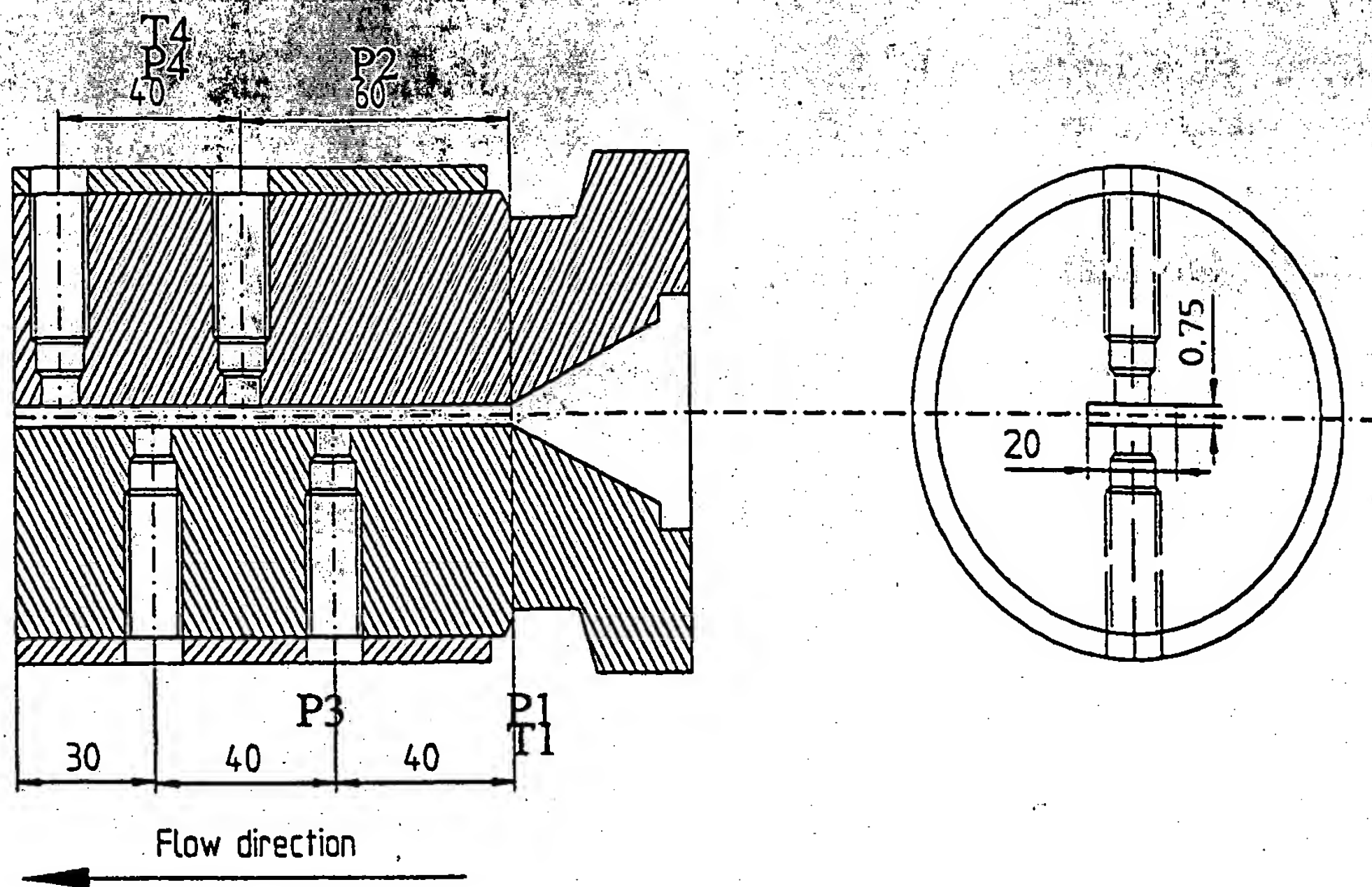
Figure 30. Slit die dimensions. Pressure and temperature transducer locations.

The L/D ratio of the die was fixed so that the flow was fully developed in the pressure measurement region of the die. The ratios were chosen from the theories according to slit die studies, as introduced in Chapter 2.1.7.

Flow channel dimensions of the slit die:

$$\text{height} = 0.75 \text{ mm} = D$$
$$\text{width} = 20.00 \text{ mm}$$
$$\text{L/D} = 147$$

The pressure transducers were located in L/D´s:

1. L/D = 53   2. L/D = 80
3. L/D = 107   4. L/D = 133

The linear line in Figure 31 indicates that L/D ratios for pressure measurements were in the fully developed region of the die and therefore suitable for further use. P_{exit} was calculated from pressures p_1, p_2, p_3, p_4 by linear regression. Other quantities, which are introduced later, were determined according to the formulas described earlier in Chapter 2.4.

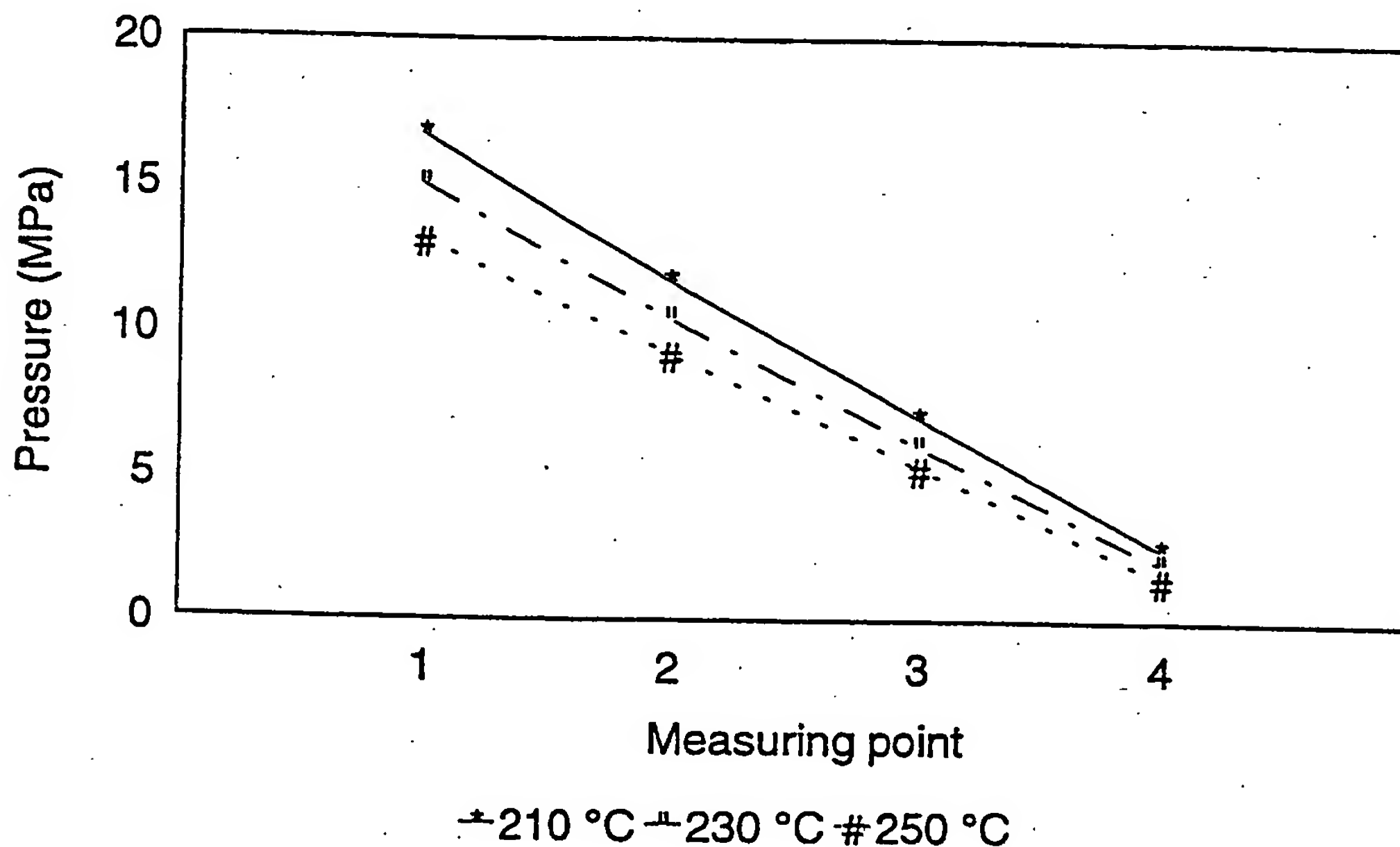Figure 31. Pressure profile in the slit die.
HomoPP

Figure 32 illustrates the correlation of viscosities between cone and plate data and slit die data, which is in agreement with Han [33]. Shear thinning behaviour of BimoPP is strong (viscosity reduction is sharper with increased shear rate). Shear rate on wall is as follows:

$$\gamma_w = \gamma_{app} /3 \ (2 + d \ln \gamma_{app} / d \ln \tau_w)$$
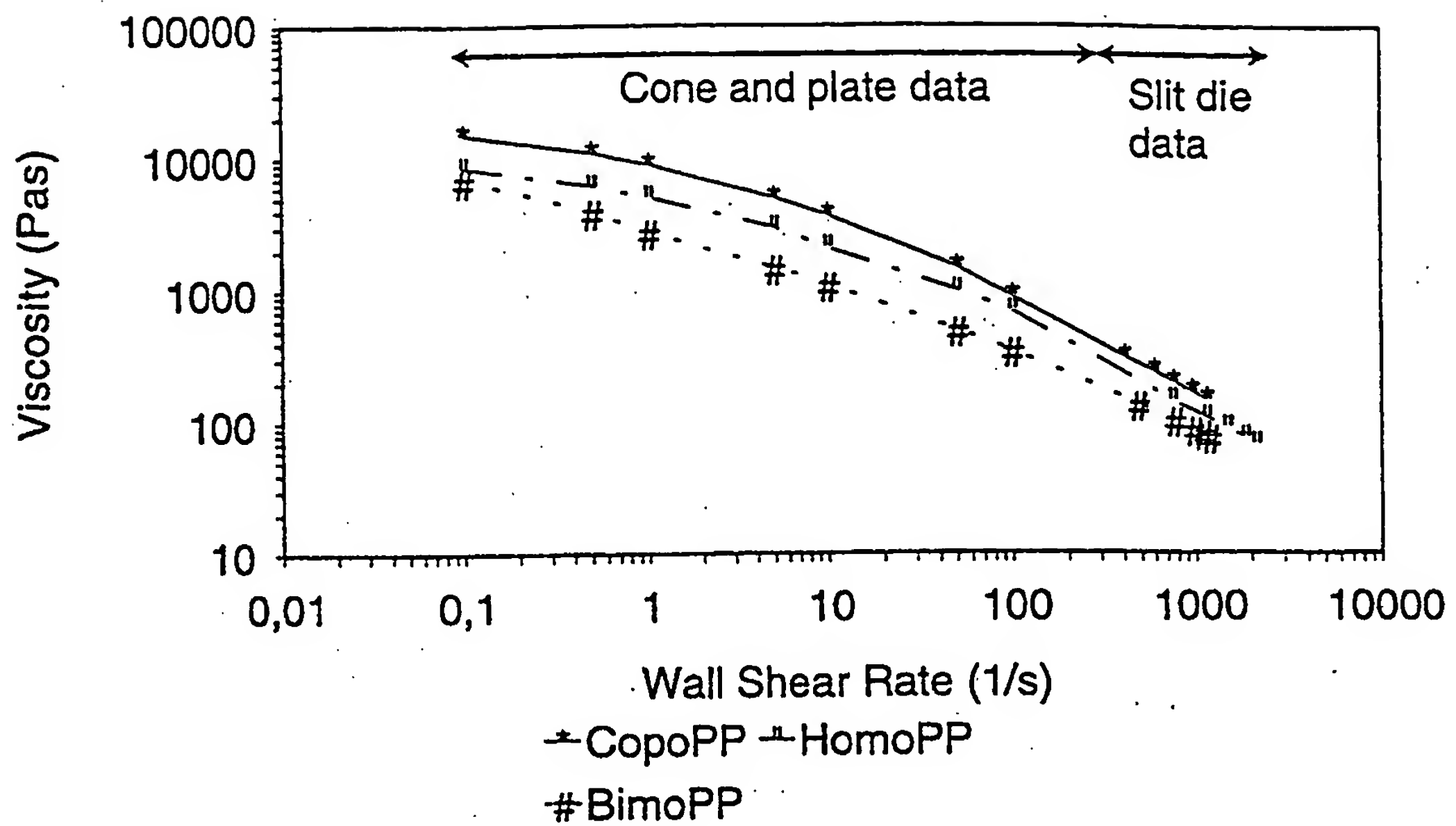
(14)

Figure 32. Viscosity as a function of shear rate. Cone and plate and extrusion rheometer data at 210 °C.

According to Figure 33, BimoPP as the lowest viscosity PP-grade produces lowest exit pressure and high viscosity CopoPP shows highest exit pressure. Exit pressure was increased in average with increased shear rate as has been proofed also in other rheological studies noted in Chapter 2.1.7. The effect of shear rate on exit pressure is nevertheless not linear, which could be a result of slipping in screw and mechanical degradation of polymer, especially at high shear rates. The extrusion rheometer apparatus and screw geometry equipped with UC mixer promotes increased shear forces, which likely cause non-linear exit pressure behaviour, which is emphasised with BimoPP type. Few studies have been conducted on the effect of molecular weight distribution together with screw design, shear effects or residence time on polymer rheological parameters. The slit die studies introduced [33, 34] produce low shear rates in average.
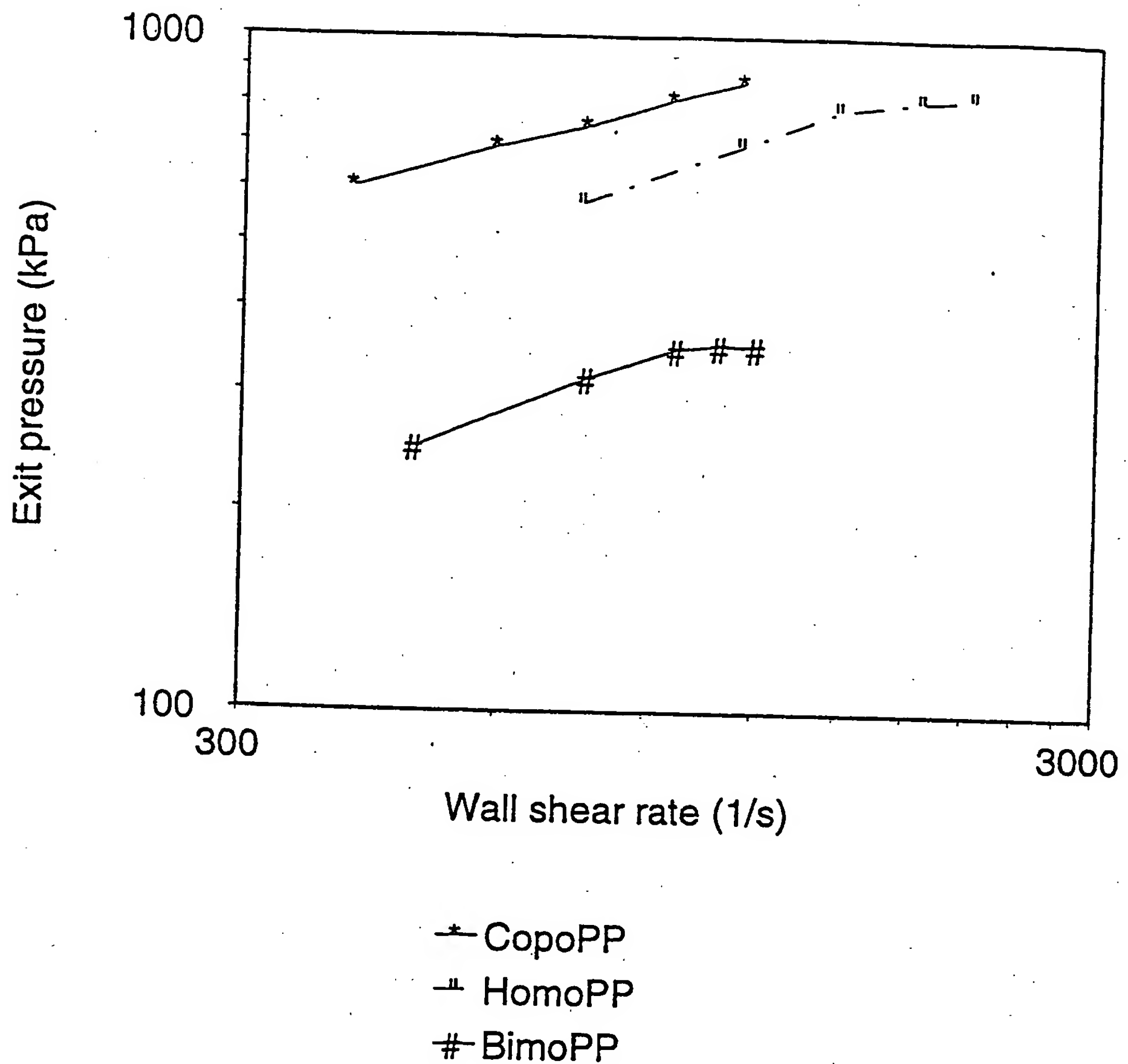
Figure 33. Exit pressure in a slit die rheometer at 210 °C.

The effect of shear rate on wall on shear stress is illustrated in Figure 34 and confirms the exit pressure data presented in Figure 34. CopoPP produces highest exit pressure and also creates highest shear stress on the wall. The dependence on viscosity is again obvious and consistent with the results presented earlier.
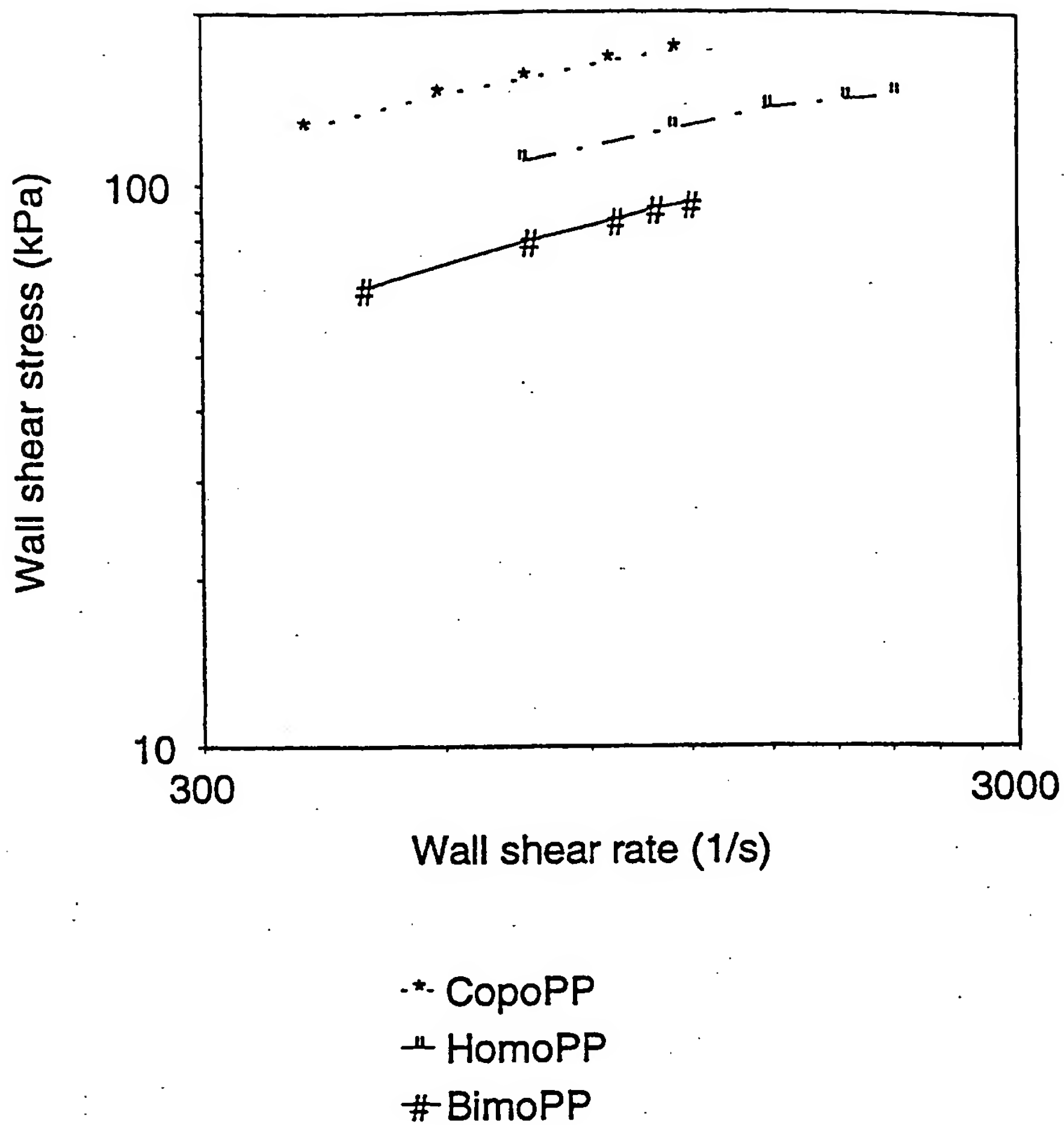
Figure 34. *The effect of shear rate on wall stress at 210 °C.*

The results discussed in slit die studies so far give the basic data to determine elastic compliance (J_e) , which takes into consideration the molecular weight distribution especially at high end weights $\overline{M}_z$ and $\overline{M}_{z+1}$. According to Figure 35 BimoPP maintains high elastic properties and therefore correlates with the theorems introduced, where high molecular weight end of molecular weight distribution increases melt elasticity [33]. Slit die rheometer studies (elastic compliance) also show equivalency with the results of cone and plate (dynamic modulus), which supports the elastic measurements with continuous extrusion rheometer.
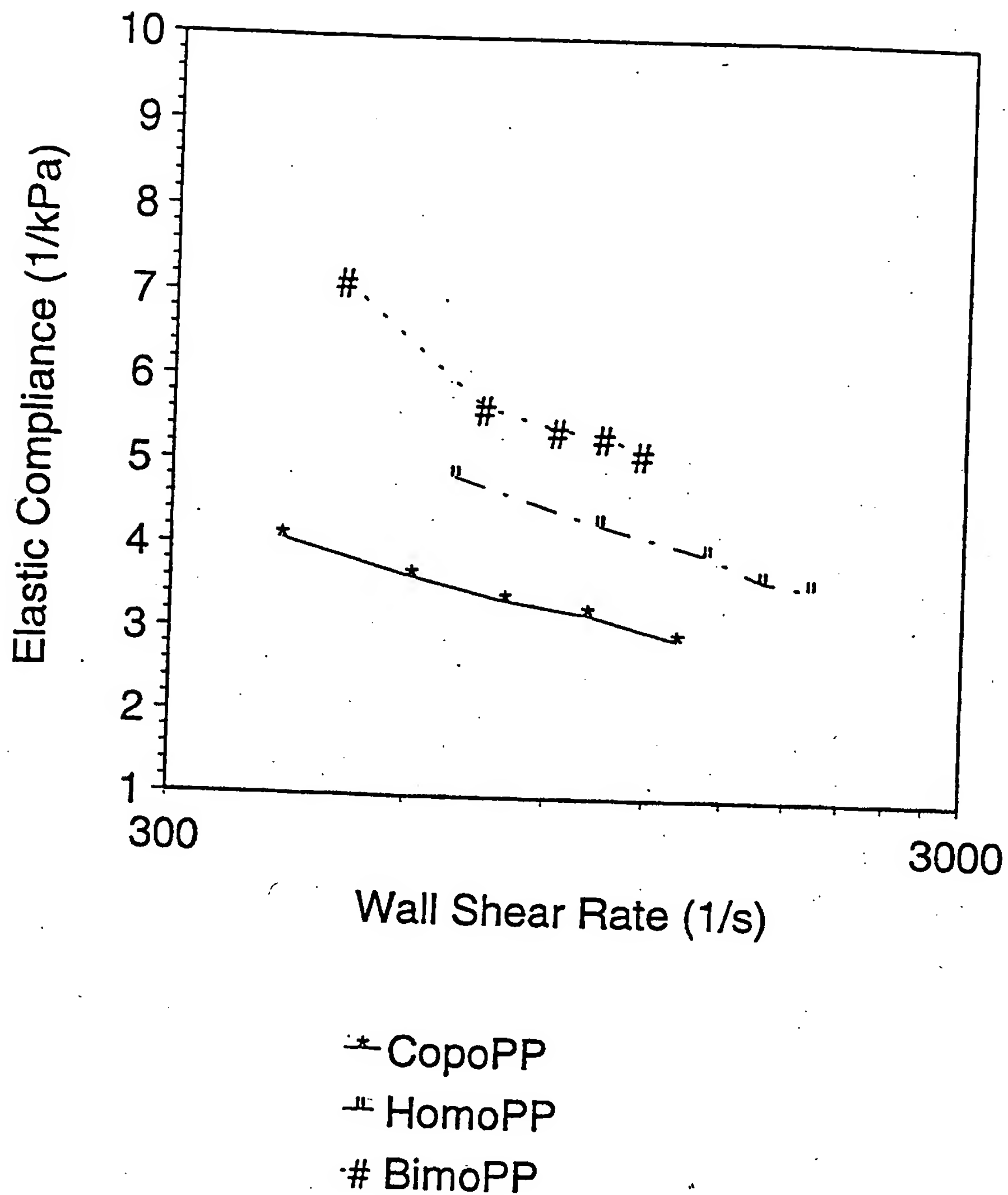
Figure 35. Elastic compliance (J_e) of polypropylenes at 230 °C.

It should be noted that molecular weight ($\overline{M}_w$ and $\overline{M}_n$) and thus molecular weight distribution (MWD) of HomoPP and BimoPP in Table 1 are nearly equal. Still, a clear difference is detected in terms of rheological properties. The increase in melt elasticity of BimoPP can again be explained through increased amount of high molecular weight end of molecular weight distribution. The data on the polydispersity index presented in Table 2 support the data on elastic compliance. The improved elastic properties of BimoPP should favours its use in extrusion foaming, where high melt strength is an advantage.

Figure 36 illustrates the final rheological behaviour of HomoPP measured by first normal stress difference at various temperatures. Elastic properties are increased with decreased temperature, which correlates with the theories of elastic behaviour and die swell introduced by Han [33]. The result also supports the experience of this study to use low temperature in extrusion foaming and especially during cell growth.
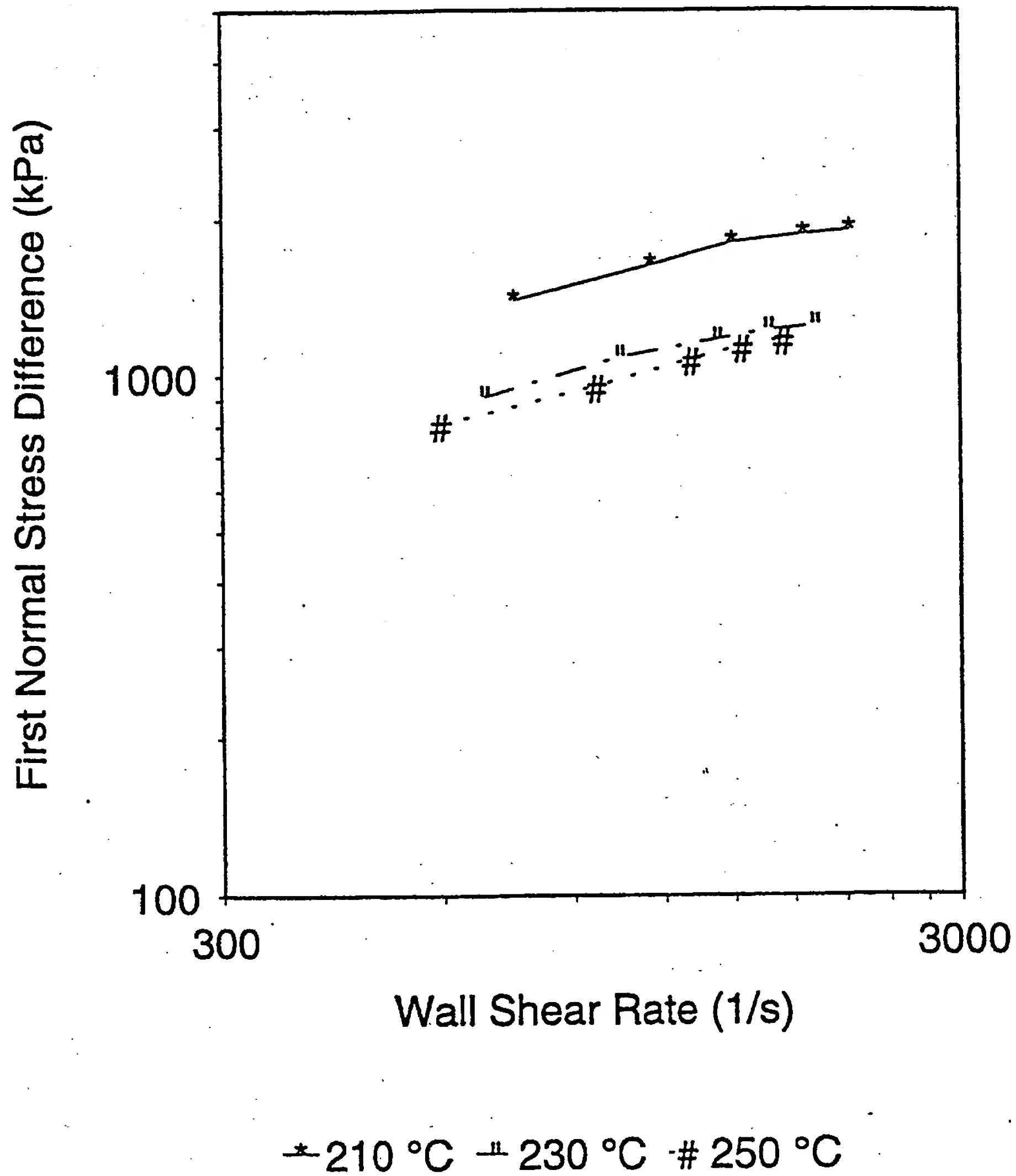
Figure 36. First normal stress difference (τ_{11} - τ_{22}) versus shear rate on wall with HomoPP at elevated temperatures.

3.4 Foam Evaluation with a Capillary Die

First foam tests were done with a capillary die to find the effects of processing parameters, polymer additives and foaming agents on the final foam structure. The principle of foaming apparatus with the capillary die is presented in Figure 37. A foaming extruder (see Figure 26) was used and the string was cooled in water immediately after die exit. The extruder was the same as that used as a foam extruder in foamed three layer sheet and film studies. Thus the melt flow history in foam extrusion was exactly the same before the capillary or three layer rotor dies.
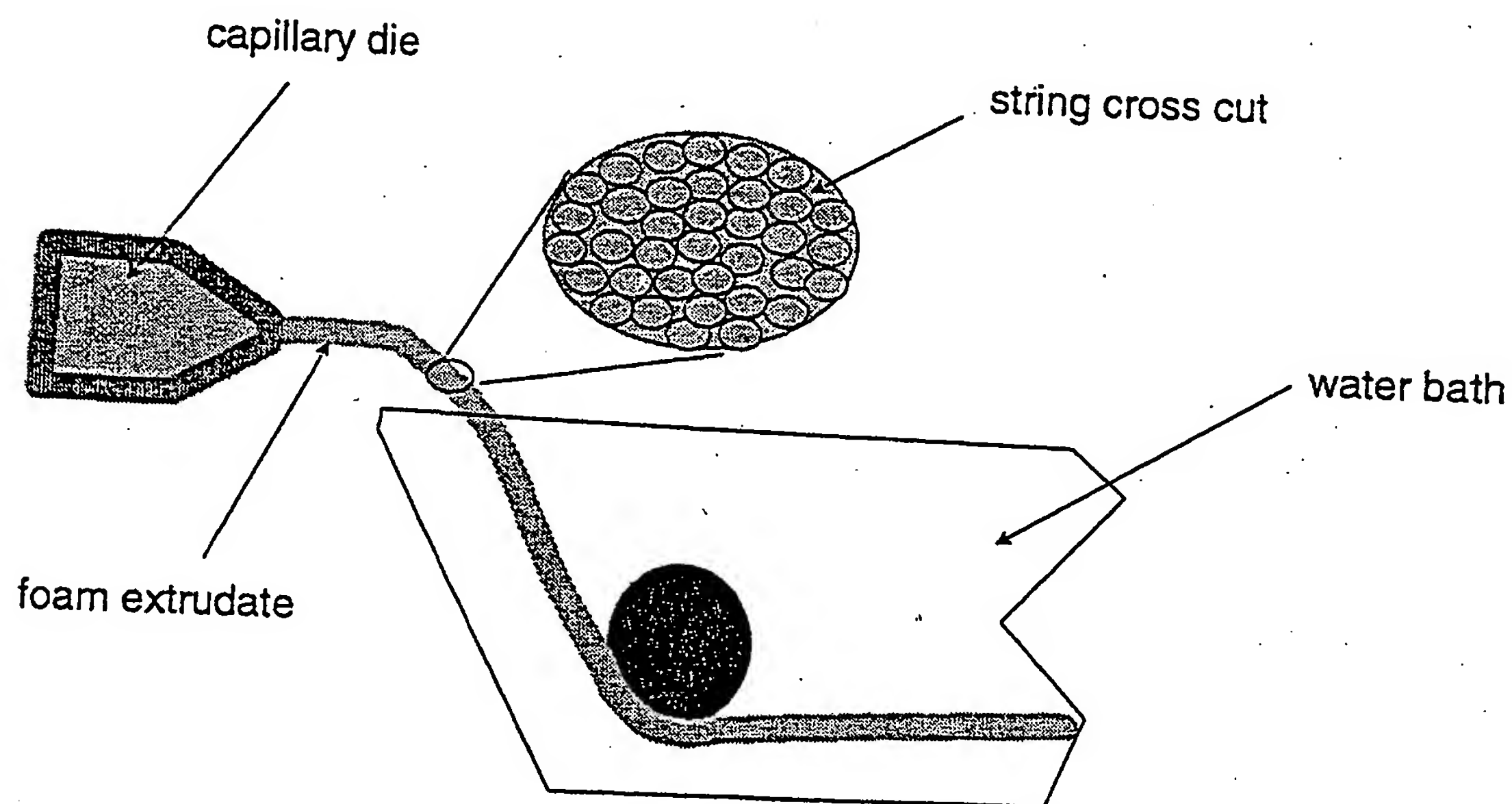
Figure 37. The principle of a capillary die apparatus for foam evaluation in extrusion.

One target was to produce a microcellular foam structure, which in this study means a cellular polymer, where the diameter of the bubbles is less than 100 μm. Nitrogen was chosen as a foaming agent, because it is inert and easy to compress at high pressure. A helium / nitrogen (5/95 %) mixture was also

tested. Helium as a small molecule size gas should create fine foam structure in polymers compared to nitrogen and carbon dioxide, which are most widely used gases in polymer foaming. In the tests with helium the structure of the foam became full of rupture. The helium diffused so fast that the melt strength of the polypropylenes was not sufficient to keep the closed cell structure. The walls between the bubbles were broken and foam extent remained low. This is consistent with diffusion theories of gases with different molecule size, their high mobility and diffusion on molten polymers [13].

The solubility of CO_2 should be about double than with nitrogen, nevertheless the pressure inside the extruder is high, which consequently needs a liquid state injection mechanism for carbon dioxide compression [3].

3.4.1 Small Particles as Foam Nucleators

The simplest idea to nucleate foam cells in PP melt was to produce interfaces inside the polymer matrix, where physically compressed gas could nucleate. Fine pulverised particles promotes the nucleation. Powders were tested by mixing them mechanically within polymer granules. This was not sufficient evidently, because the foam structure was unhomogeneous. The diameter of the foam bubbles was large and the foam extent remained low. Three particle mixtures; Na-bentsoate, talc powder and PTFE powder with polypropylene acted as nucleating agents, especially when surface tension was lowered with surface active additives, silicones. Nitrogen gas nucleated into the low surface tension boundary layers. The temperature in the extruder never exceeded 220°C, which enabled the use of PTFE powder as a particle nucleator. Na-bentsoate and talc are also used as nucleation agents for crystallising in polypropylene. With a rotating mechanical mixer fine powdered particles form agglomerates between the polymer granules which nucleate the foam cell, but their density in a polymer matrix is too low to produce a microcellular foam. This was especially a problem with PTFE powder which dielectric constant is very high and the powder produces static electric charged agglomerates in during mixing and before extrusion. The agglomerates can nevertheless be partly separated by effective mixing in extruder and with optimised screw geometry.

Small particles as foam nucleators were also tested together with the chemical foam nucleators. The results are presented in Chapter 3.4.3.

3.4.2 Interphase of Another Polymer as a Foam Nucleator

Besides solid particle interface in molten polymer, the interface can also be formed by crystallised polymer. The idea is to melt the secondary polymer in the extruder together with the polymer matrix, mix it effectively and cool it already in the die so that an interface is formed for foam nucleation. Because of high melting point of polypropylene on average, it is difficult to find a secondary polymer which would crystallize at the extrusion temperature of polypropylene.

POM, PET and PTFE were tested for PP without a successful result. It is obvious that the compatibility and surface energy of polymers controls the foam nucleation on a crystallised surface. Closed die cooling and a double extruder would probably be the most suitable for two phase foam nucleation. Foam film manufacturing on this principle was excluded because of the sensitivity of the process in general.

Instead of using PP, a successful test to prove the main idea of nucleation was done with 5 % polyasetal in polyethylene. The die exit temperature had to be set as low as 140°C, which disturbs polymer flow and thus limits extrusion conditions. The temperature profile in extruder is illustrated in Figure 38.
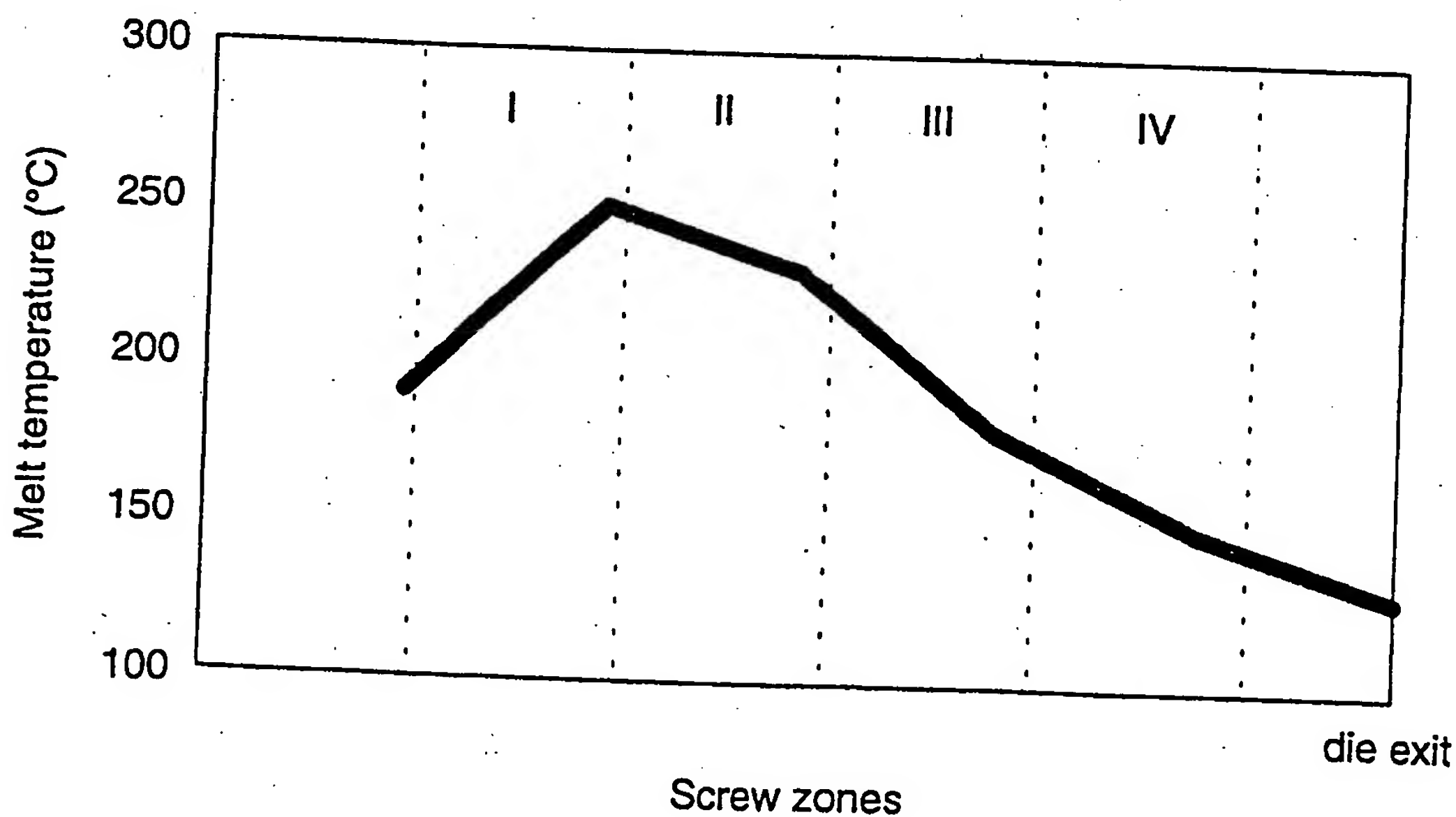

Figure 38. The temperature profile for polymer secondary phase foam nucleation in extrusion. A blend of PE/POM (95/5 %).

3.4.3 Chemical Foam Nucleating Agents

Chemical foam nucleating agents are the most widely used foam nucleators in polyolefins. They dissociate chemically at a certain temperature leading to a small amount of released gas to create a foam to nucleate. This study showed in general that without an external foaming agent (nitrogen), 50 % foam extent in PP was a maximum, and the dosing of the nucleator had to be around 0.5 %.

In this study chemical foam nucleators were used mainly only in very small amounts to create cell embryos for physically compressed nitrogen gas. The dosing of the nucleation agent can be reduced to 0.1 - 0.15 % of weight. The foam extent can be increased up to 90 % depending on the polymer. Economically physical foaming is also cheaper. It was also noticed that with chemical foaming the walls of cells are easily broken and microcellular structure is more difficult to achieve. The reaction with chemical foaming agents is often too explosive, complete and less controllable compared to bubble growth by externally dissolved gas.

The foaming agent in this study was a masterbatch of polyethylene and chemical foam nucleation agent based on sodium bicarbonate. The dissociation reaction of the nucleator is endothermic. The foam nucleating agent has two decomposition temperatures (Figure 42), which significantly helped the process control in extrusion. Foam bubble growth was more controllable by a set of temperatures, and the final structure also resembled closed cell, which is introduced in Chapter 3.4.3.1.

Perhaps the most widely known exothermally decomposable nucleation agents, azo-compounds were also tested. The foamed extrudate was more uncontrollable and often unreacted parts stayed in the final product, which made it yellowish and disturbed the film blowing. The use of premixed masterbatch usually helped the decomposition to be complete. The cell size with azo-compounds was large, and the walls of the cells were easily broken. The bubble growth just after the die exit was too rapid to bear for cell walls and the temperature control was limited as has also been noted in other studies [66, 77].

Table 3. Density and cell size of three different polypropylenes in foam extrusion with a capillary die. The amount of endothermic chemical nucleation agent was 0.1 %. Nitrogen was fed externally into the extruder.

POLYMER	DENSITY	BUBBLE SIZE (μm)
HomoPP	0.51	70-90
BimoPP	0.22	80-120
CopoPP	0.57	80-120

Table 3 shows the density levels obtained from the structure of three polypropylenes, when cells were unbroken (closed cells).   Processing parameters were set so that the extrudate flow was smooth and homogenous. Foam extent can be increased if the gas compression pressure is increased, but it caused the break of cell walls as will be discussed further. The foaming properties of BimoPP were outstanding compared to the others. The structure of the foam looked like honeycombs, where cell walls had been stretched in a great extent (Figure 39).
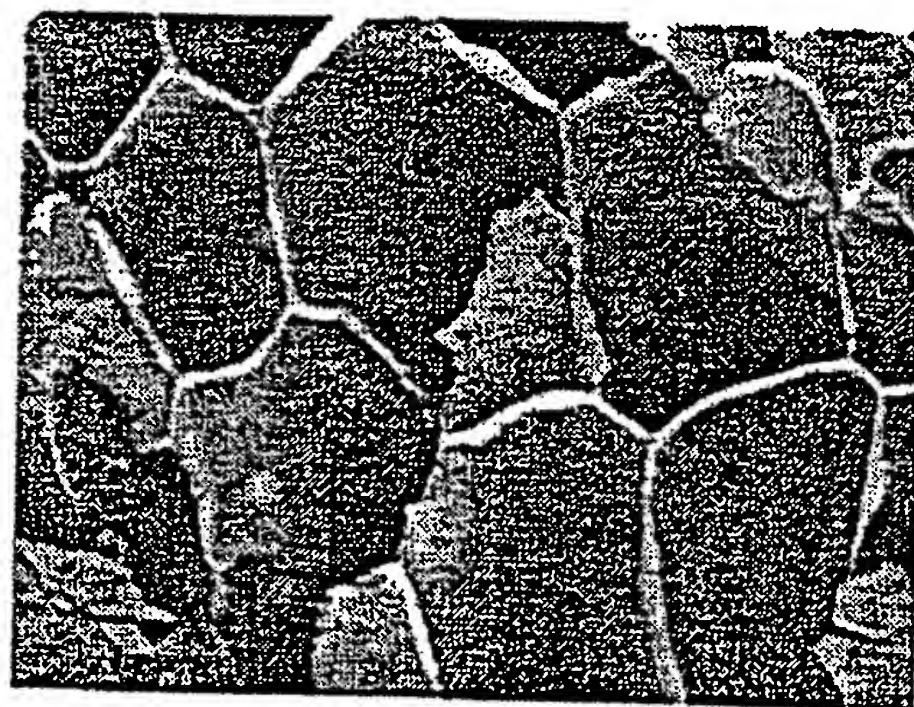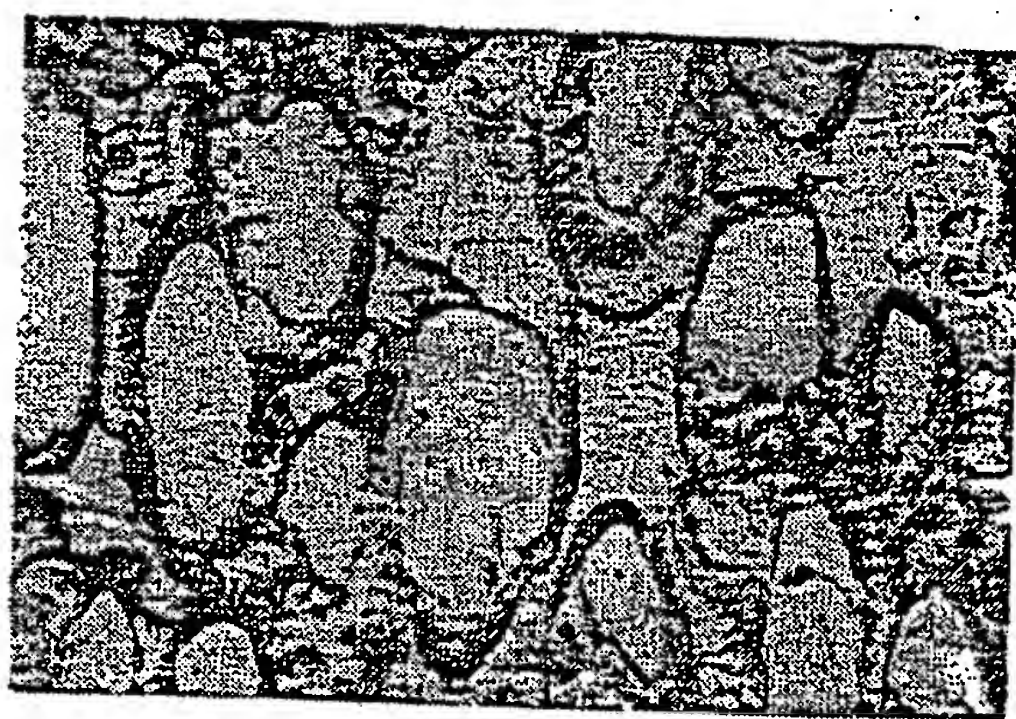

A)

B)

Figure 39. A) Cross section (microscope) of foam structure produced by extrusion in traditional slurry processed polypropylene (HomoPP). 200 X.
B) Cross section SEM picture of the honeycomb foam structure produced by extrusion in bimodal processed polypropylene (BimoPP). 200 X.

3.4.3.1 The Effect of Temperature on Foam Structure

The effect of temperature on cell size and foam extent is introduced in Figures 40 and 41. In general it was chosen to keep the temperature level slightly above the decomposition temperature of the nucleating agent. High extrusion temperature improves the plasticising effect, but inhibits stabilisation of the expanded extrudate.

As Figure 40 shows, the foam cell size is increased when the temperature is increased. The increased cell size is in correlation with decreased viscosity and has been established by other studies noted in Chapter 2.1.2. The foam structure can be controlled more easily at low extrusion temperature, because the elastic behaviour of the polymer is at its highest, as illustrated in Figure 36. The higher the temperature is the more easily the cell structure is ruptured, which is in correlation with other analyses and which has especially been illustrated with low melt strength polymers such as polypropylene [29, 30]. The highest foam extent was reached at a temperature of around 200 °C, which has been described in Figure 41. It has to be emphasised that the foam extent results were measured when the sample remained closed cell. A temperature of more than 210 °C was adequate to collapse the cell walls and closed cell structure is hard to achieve.
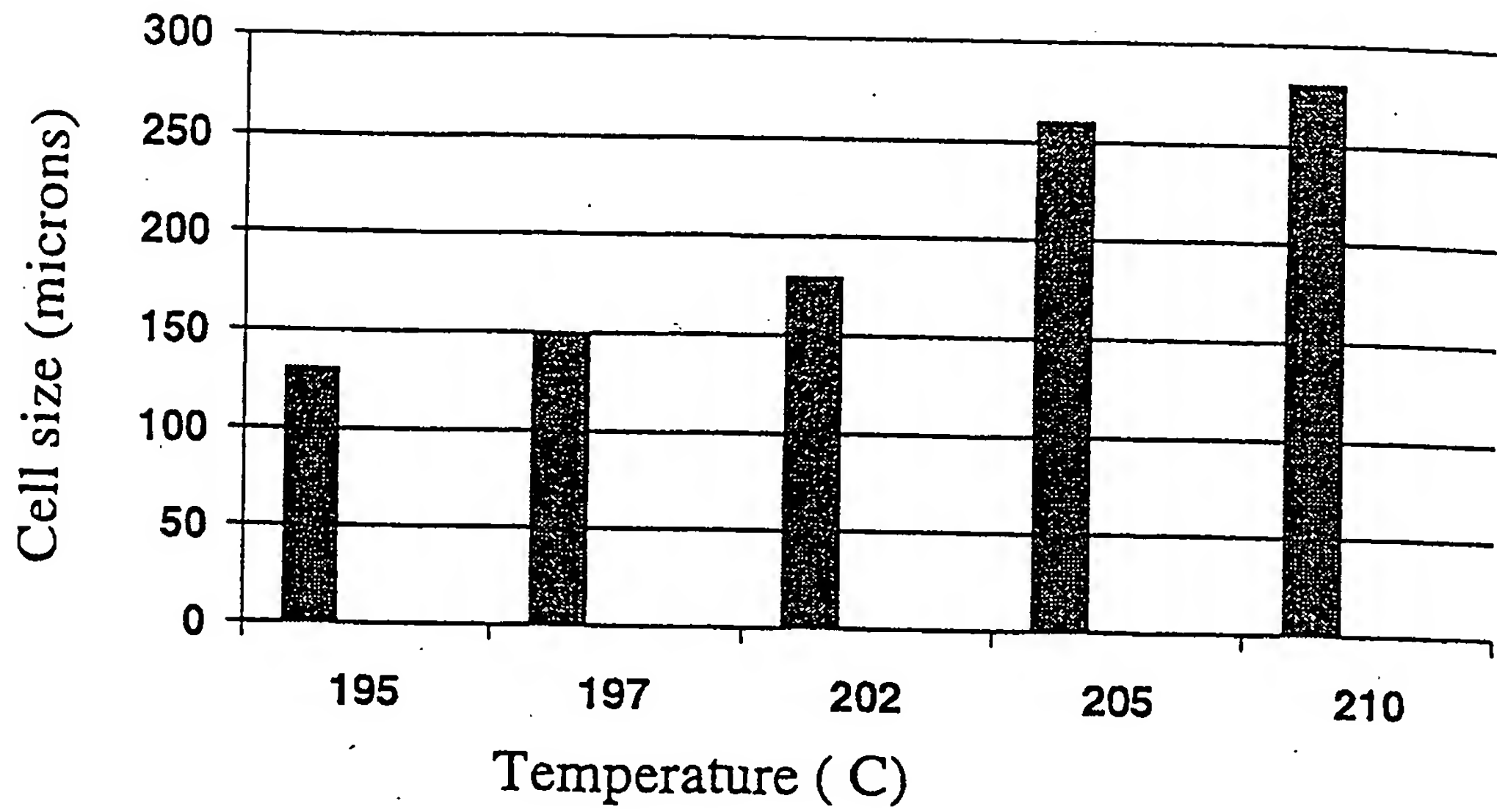
Figure 40. Bubble size versus extrusion temperature with a capillary die apparatus.
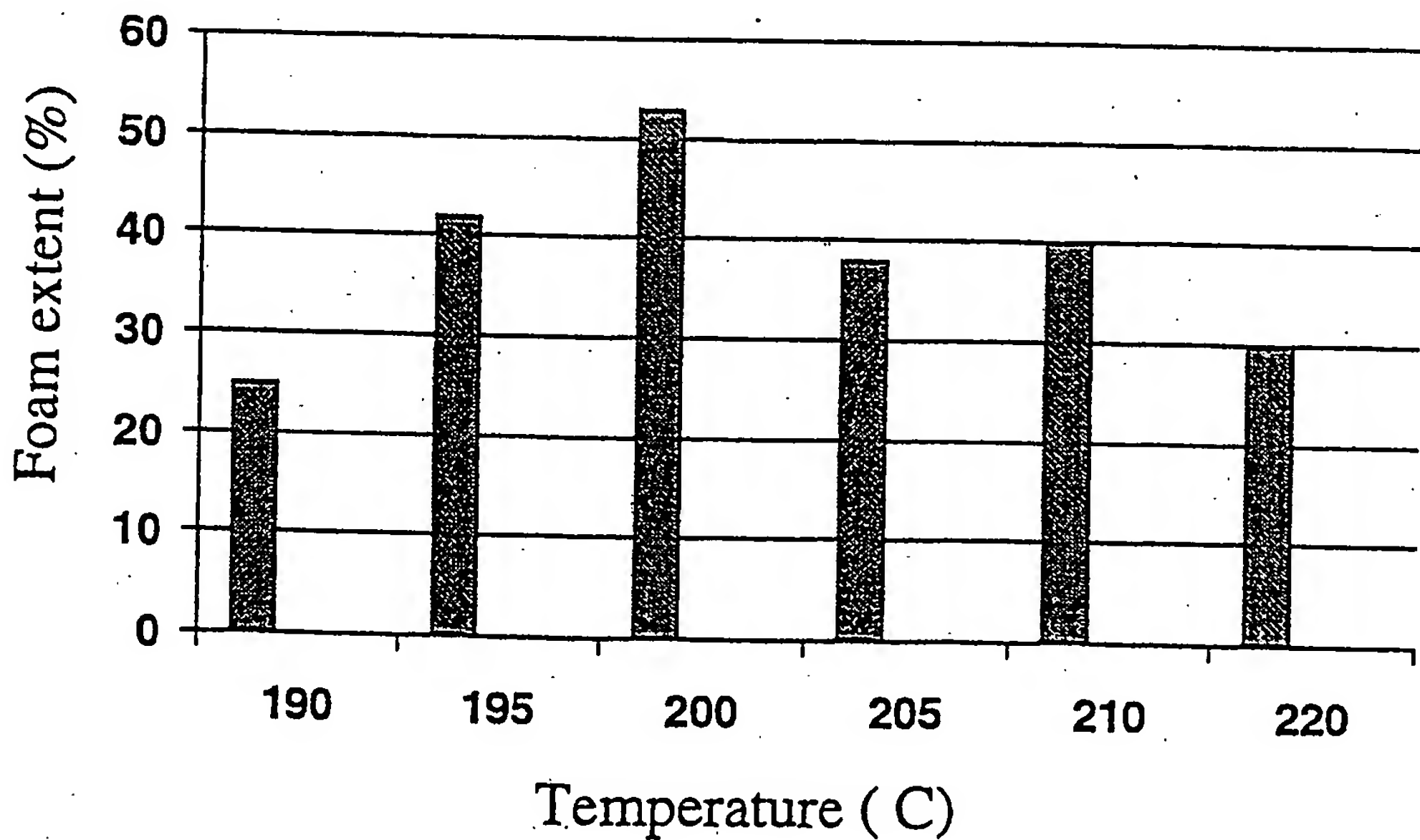
Figure 41. Optimised extrusion foaming temperature for chemical foam nucleating agent.

The critical temperature can also be explained by DSC analysis presented in Figure 42. The first endothermic peak is obviously the melting point of PE-LD of the masterbatch and the second peak is the first endothermic chemical decomposition temperature of the nucleating agent. At the second temperature peak (179 °C) the plasticizing effect is not adequate to form homogenous cell structure until the temperature reaches 198 - 205 °C. At extrusion temperature in third peak (215 °C) viscosity reduction of polymer together with the second decomposition reaction of chemical nucleating agent ruptures the foam structure.

It should be noted, that the solubility of nitrogen gas in polypropylene likely increases slightly with increased temperature [3]. The temperature variation in this study is nevertheless narrow, thus the effect of solubility on these results could be considered insignificant.
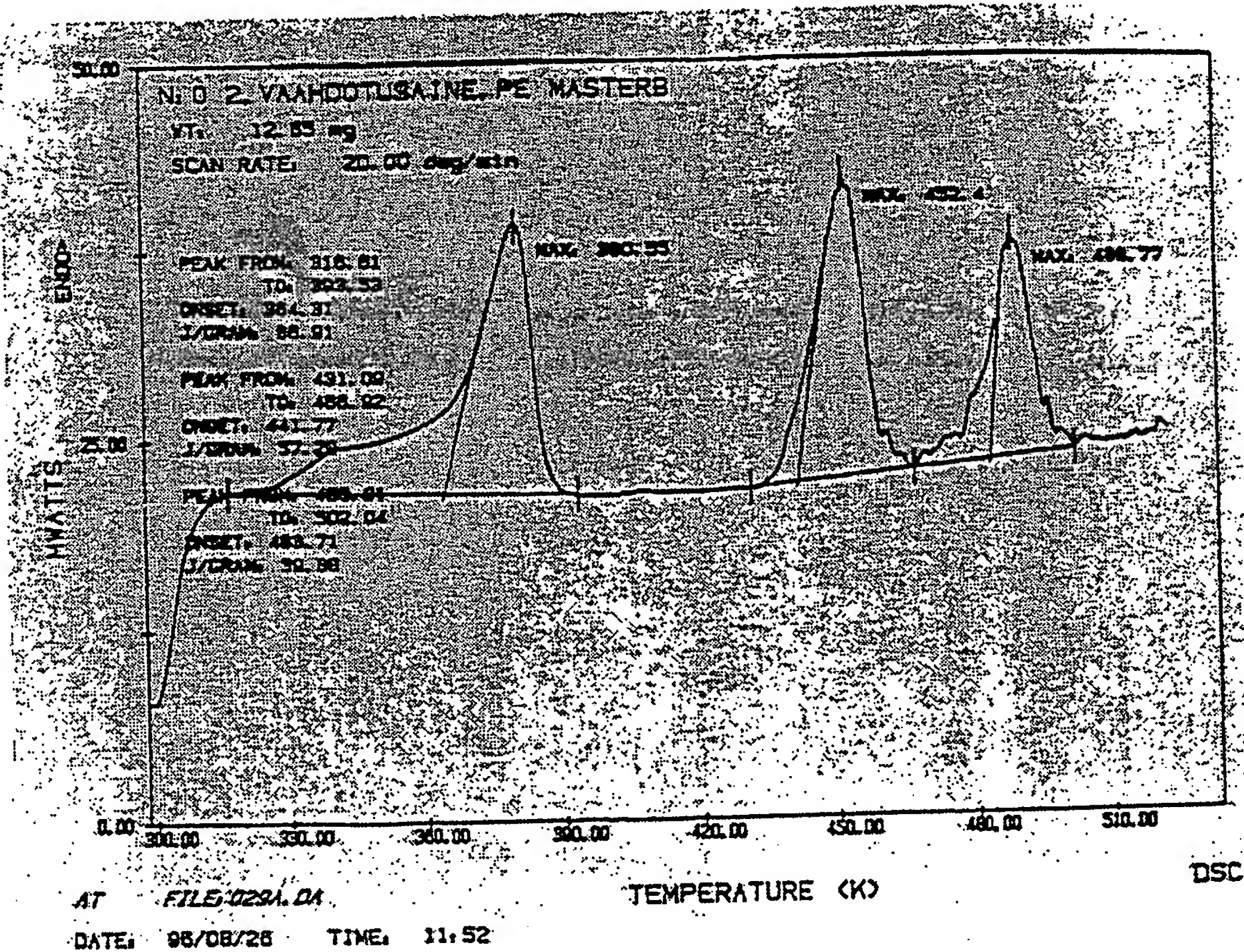

Figure 42. DSC diagram of the PE-LD masterbatch.

3.4.3.2 The Effect of Gas Pressure on Foam Structure

The effect of gas compression pressure on foam extent was difficult to measure during extrusion because of very narrow tolerance in melt stretching of polypropylene on average. Still, it was clearly observed and unambiguous that the increase in gas compression increased the amount of foaming gas and foam extent increased correspondingly as has also been discovered in the literature [2, 10]. Foam bubbles grew in diameter at the same time as expected. Foam expansion started rapidly after the die exit when the nitrogen saturation pressure was reached and external pressure was reduced. If the amount of gas was still increased, the structure collapsed quickly. This can be explained through low melt strength properties of polypropylene, which reduces the control region of foam extent. However, foam extent can apparently be increased by increasing the gas pressure, but destroying the closed cell foam structure. Only a large cavity between the skin layers is left due to collapsed foam bubbles. The tolerance was clearly wider with high melt strength grade BimoPP. Figure 43 illustrates the bubble formation and growth in extrudate, where the change in structure of PP foam is rapid, when the amount of foaming gas (foaming agent) is increased. A common problem in PP foaming can be observed in Figure 43b), where bubble collapse has started.
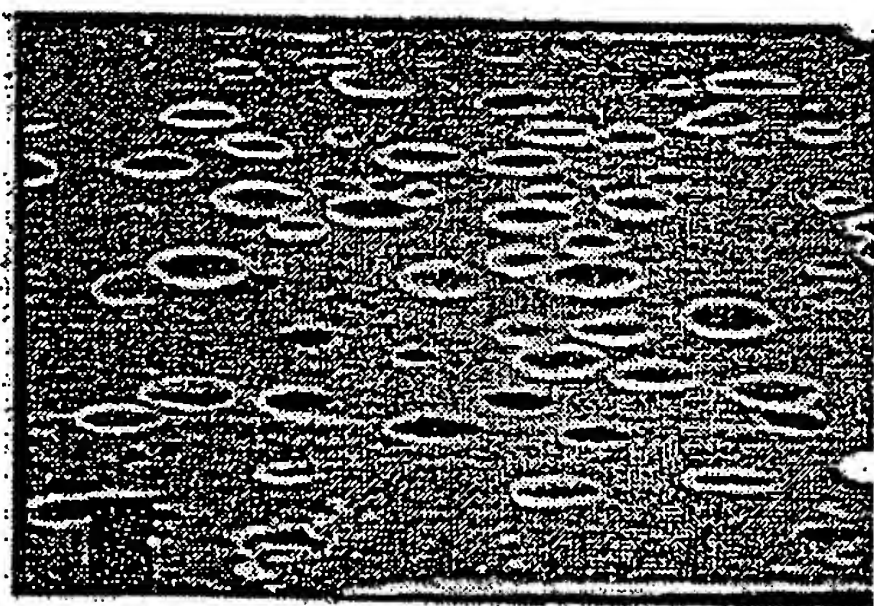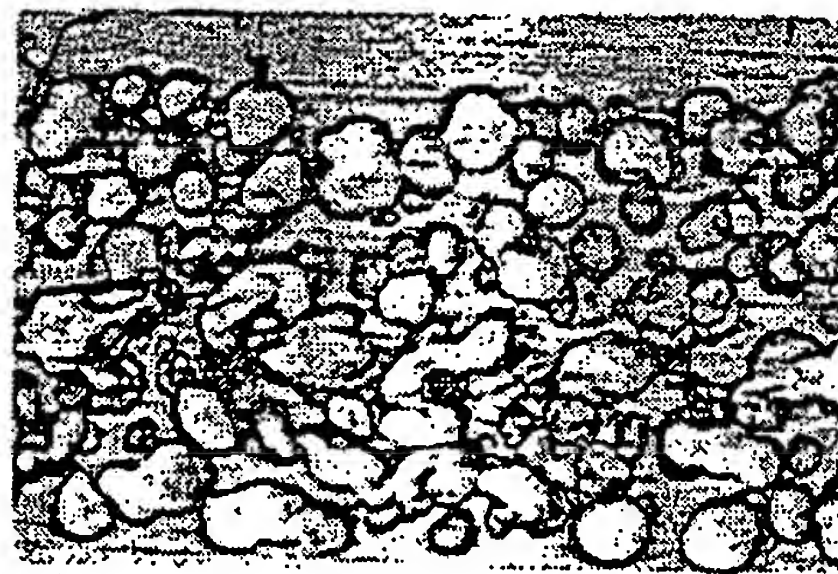
a)   b)

Figure 43.   Typical foam structure of polypropylene extrudate with
a) low gas load - low foam extent (75 X)
b) high gas load - high foam extent (bubble collapsing)(75 X).

3.4.3.3 The Effect of Melt Pressure on Foam Structure

Polymer melt pressure inside the extruder could be modified with screw speed, temperature, adjustable die lip and viscosity of the polymer. According to test runs done in this study, polymer pressure in the extruder did not significantly affect foam bubble size or foam extent, when other characteristics were kept constant. Tests were done from 5 - 12 MPa by changing the screw speed. The only noteworthy attention was paid to the solid section of the extrudate, which could visually be observed and surface roughness. When extruder pressure is low, foaming starts already inside the cylinder, resulting in rough surface on extrudate. When the pressure is increased, the solid section increases after die exit resulting in smooth surface. The result is consistent with Kraynik [67] and what has been presented in Chapter 2.1.7.

According to Table 4, polymer temperature together with the gas saturation pressure dominates the extrusion foaming of polypropylene. The optimisation of gas saturation pressure and polymer melt pressure is dependent on the viscosity of PP and melt stretching properties. Therefore the correlation of pressure on foam structure could better be observed from the effect of polymer viscosity on cylinder pressure i.e. melt pressure.

Table 4 shows the results from the studies where pressure in the extruder was changed by changing the temperature. Foam structure was kept homogenous based on the bubble size, foam uniformity, foam extent and extrusion flow continuity, and it could be controlled with the amount of blowing gas (p_g). It can be seen that changes of 5 °C can be critical in the created foam extrudate. When the temperature is around 200 °C, the foam bubble size can strongly be reduced and foam extent is increased. When the temperature rises, the flow is getting better to bear higher amount of nitrogen, which nevertheless escapes from the low viscous extrudate, causing increased bubble size and bubble collapse. This is because the solubility of the nitrogen increases with increased temperature and also the plasticizing effect is improved at temperatures over 200 °C. CopoPP has the highest MFI and created the highest cylinder pressure, which resulted in less dramatic increase in foam bubble size. It is obvious that higher viscosity retards bubble growth immediately after external pressure drop. The ability to store nitrogen gas to create a closed cell foam structure was clearly highest with BimoPP, which is indicated by the ratio of p_g/p_m. The ratio of

of blowing gas pressure on melt pressure in the cylinder increases when temperature is raised, which can obviosly be explained from the viscosity reduction.

Table 4. The effect of temperature, gas pressure (p_g) and melt pressure (p_m) on foam structure with a capillary die.

Material	Temperature (°C)	p_g/p_m	Foam extent (%)	Bubble size (μm)
HomoPP	200	2.25	52-54	60-80
	205	2.57	38-43	80-100
	210	3.20	30-34	>100
BimoPP	200	3.20	75-80	>100
	205	3.50	70-75	>100
	210	4.40	66-70	>100
CopoPP	200	2.75	35-40	50-120
	205	3.25	30-32	50-120
	210	3.30	28-30	50-120

A notable observation was made when the foam trial was finished by stopping the extruder suddenly during foam extrusion and letting the extruders cool overnight resulting in a fine microcellular foam structure for a very short period of time, when extrusion was started again in second day. This could be explained through improved gas solution in the polymer and prefoamed extrudate in closed space, which makes tightly packed cells possible before the final foam expansion as described by Baldwin et al. [69]. The solubility of nitrogen may increase also in the long period of time to give abetter foam result, but few studies is made in this field.

3.5 Foam Studies with a Three Layer Rotor Die

The influence of process parameters on foaming and the determination of the polypropylene material combination best suitable for extrusion foaming was first defined with the capillary die. Foam processability into a foamed tube or biaxially oriented foam film was afterwards determined with a three layer die. The aim was to reach a fine microcellular closed cell foam structure (bubble diameter less than 100 μm) with highest possible foam extent in foamed tube and to stretch this finally into an oriented foam film.

As a general comment, the three layer rotor die developed for the foaming studies destroyed the spiral marks of the extrudate and the final structure was visually homogenous. Immediately when the rotors inside were stopped, the spirals appeared from the cog mixing centre. This supports the basic idea of effective mixing in foam extrusion and destructive effect of the thermal and flow history of a viscoelastic material.

3.5.1 Polypropylene Foam Extrusion with Chemical Nucleators

In solid film blowing the polymer temperature is kept lower and viscosity higher compared to flat film extrusion. The film blowing is sensitive to the blowing pressure inside the bubble (MD/TD -orientation) and the bubble must be raised in form, which is complicated if the viscosity is too low. As this study presents, choosing temperature in extrusion foaming is often more complicated and limited compared to solid polymer extrusion. Commonly it is a question of material choice and properties connected to screw and die design ending in foam stabilisation. Besides if the polymer is foamed, it makes the structure even "softer" in temperatures higher than melting point, so the temperature-viscosity relationship is even more emphasised.

According to the evaluation made by the capillary die, the same endothermic nucleating agent was used in the further studies with the three layer rotor die.

Table 5. Foam extents from the foam studies in three layer extrusion.

POLYMER	TUBE DENSITY	FILM DENSITY
HomoPP	0.52	0.42 - 0.48
BimoPP	0.22	0.27 - 0.45
CopoPP	0.55	0.46 - 0.52

Table 5 presents the foam extent (density) of three different PP qualities. In terms of processability HomoPP was the most stable in foam film blowing. The foam extent of CopoPP was almost equal to HomoPP, but the foam cells were much bigger, which led to rough surface. This is already detected in Table 4, when the base properties in foaming were examined with a capillary die. Also, film blowing of CopoPP was more sensitive to rupture. Copolymer morphology did not yield better melt strength properties in foaming as was first expected and which was further detected in rheological studies. A temperature sensitive process both in foaming and biaxial orientation does not favour the use of polypropylene copolymer with an ethylene fraction.

BimoPP gave the highest foam extent values in tube and film foam extrusion. The foam structure was uniform and closed cell. The most critical consideration in biaxial orientation was temperature control, which is logical in foamed structures. The tube cooling should be effective in order to reach the same temperature from the surface of the cooled skin into the middle of the highly expanded, foamed and insulating middle layer. Temperature should again be raised in the reheating oven to the orientation temperature (near 140 °C) through the tube thickness. Therefore the semifinished product, foamed tube, had to be stretched thin before successful film orientation.

As Table 5 indicates, the foam extent increased (density decreased) when the foamed tube was stretched into an oriented film. Under effective cooling on the cooling mandrel, an interior pressure may be encapsulated in foam cells. The softening of the cell walls in reheating enables pressure equilibrium between cells and atmosphere inducing cell expansion. The walls of the bubbles are

already stretched thin during foam expansion, which promotes cell growth during reheating.

The behaviour of BimoPP was exceptional. The density of the foamed tube was much lower compared to other types. The structure had to be flattened in reheating stretching so that the bubble structure was damaged and the gas penetrated away from foam cells. Temperature uniformity in the stretching of a highly foamed structure is emphatically problematic as described earlier. Another explanation could be the upper nip, which makes MD orientation and which had to be under high pressure to keep the blowing air under the nip. The nip may also partly flatten and damage the foam cells, and increase the escape of foaming agent.

Figure 44 illustrates the foam film where lenslike cells are stacked on top of each other to make the film opaque. It should be noted that skin layers are thick in comparison to film thickness. This is appropriate to support the film stretching, which otherwise would be probllematic i.e. stretching of highly drawn thin cell walls is limited in film blowing. This can be supported by Kraynik et al. [37], who presented a clear deformation of hexagonal foams already at low stretching ratios.

Crystallinity of the BOPP film was increased during orientation about 5 % on average, which is also attested in literature. Figure 45 illustrates the DSC double peak that appeared concurrently in film blowing. The higher the orientation was the easier the double peak is to see. This is said to be derived from changes in crystallinity and reorganisation of the morphological structure [73]. Foam film is probably more sensitive to reorganisation due to very thin (about a micron) cell walls, which could be understood as very thin films i.e. the orientation ratio versus film thickness (the wall of an individual foam cell) may increase rapidly into high extent - microfibrills.
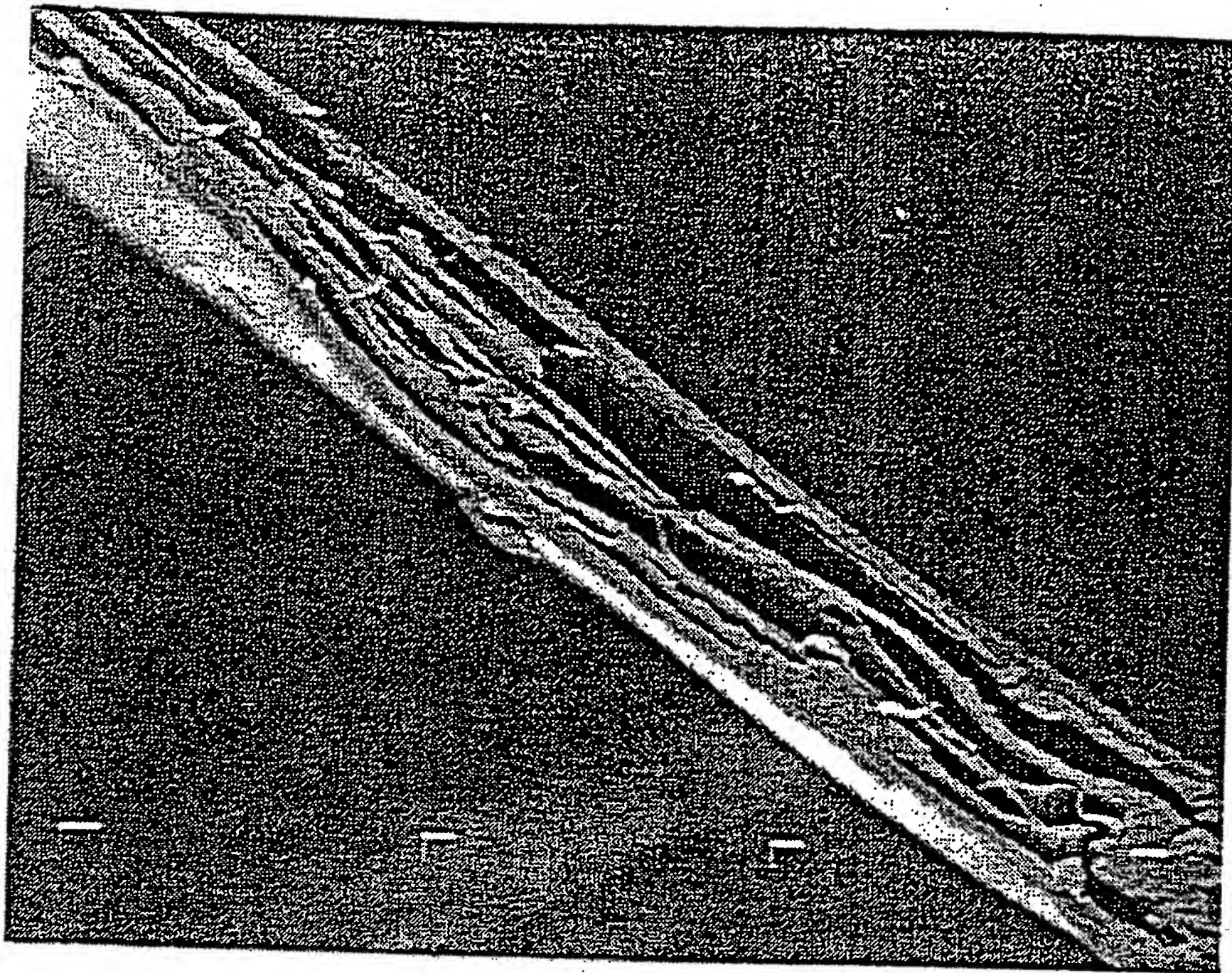
Figure 44. SEM cross cut picture from BOPP foam film.
Film thickness 60 μm

The visual opacity of foamed BOPP films did not reach the level of cavitated films, which is evident when Figures 45 and 7 are compared. Layers on top of each other are approximately one third from the cavitated one, which greatly effects both opacity and stiffness of the film. It can be postulated that the smaller the foam bubbles are, the more interlayers will be produced and the stiffer the film, which Table 6 also illustrates. It should be noted that the formation of the foam bubbles or cavities is different. Cavities are produced in commercial films during orientation, which respectively increases the orientation of the interlayers. In BOPP blown film foam bubbles are produced before orientation and therefore the film orientation is concentrated on surface skin layers, and the foam bubbles will be mainly deformed in shape (flattened, [37]). Barrier properties (Water vapour transmission rate) are also reduced in blown foam films, which supports the last statement. In this matter Ward et al. [78] indicated the increase in barrier properties with increased stretching ratio.

Table 6. Tensile strength at break, E-modulus and water vapour transmission rate in foamed (BimoPP) and cavitated (commercial) BOPP films.

	FOAM FILM	CAVITATED FILM
Film thickness (μm)	30	30
Weight per square (g/m³)	12.5	20.7
MD Tensile strength at break (MPa)	67	80
TD Tensile strength at break (MPa)	24	170
MD E-modulus (MPa)	774	1210
TD E-modulus (MPa)	104	2090
Water vapour transmission rate (g/m² * 24 h)	$\approx$ 10	$\approx$ 6

Overall densities less than 0.4 g/cm³ were difficult to achieve in thin films by film blowing technology. One way to increase the foam extent would be the decrease in cell diameter, which could increase the tolerance in nip rolls. The idea of a very fine closed cell microcellular BOPP film has led to an expansion technology where densities less than 0.4 g/cm³ can be achieved in prefoamed or cavitated films and the structure is simultaneously stiffened [71].
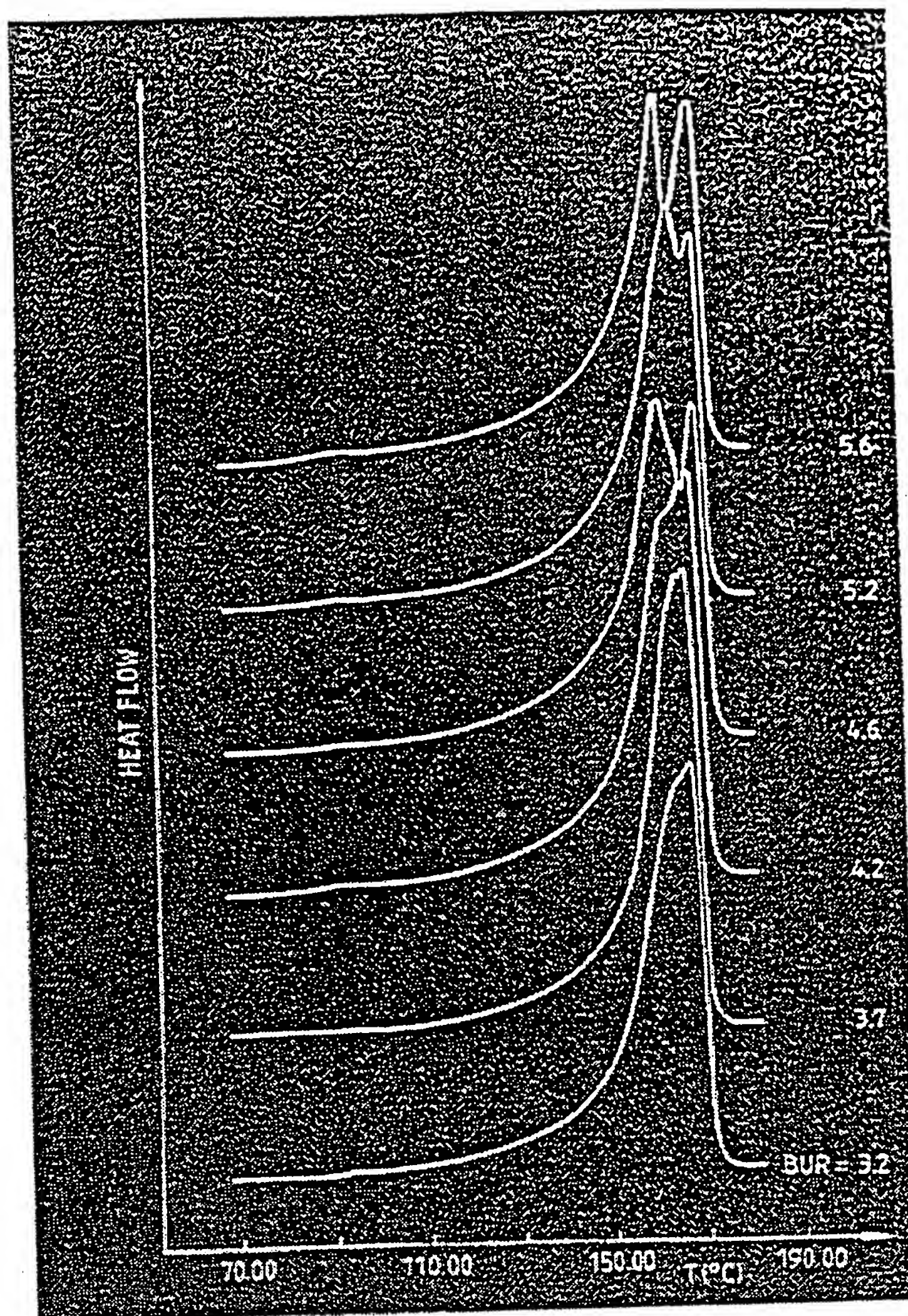
Figure 45. DSC diagram of BOPP foam film in different orientation ratios (BUR).

3.5.2 Polypropylene Foam Extrusion with Solid Particle Nucleators

Foam nucleation with solid particles was not satisfactory on average in terms of cell size as described in capillary die tests. The effect of solid particle nucleators with the presence of chemical foaming agent on foam structure (cell size, cell density, foam extent) of tube and biaxially oriented film was further studied and the results are illustrated in Table 7.

Table 7. The effect of solid additives on foam structure with CopoPP
*PP + 0.15 % Chemical Foaming Agent (CFA)*
PP + 0.15 % CFA + 0.5 % Talc
PP + 0.15 % CFA + 0.5 % PTFE powder

MIXTURE	TUBE /FILM	THICKNESS (μm)	CELL SIZE (μm)	DENSITY (g/cm3)
1.	TUBE	620	80 - 120	0.62
	FILM	35		0.58
2.	TUBE	680	80 - 120	0.56
	FILM	40		0.52
3.	TUBE	700	7 - 110	0.54
	FILM	35		0.48

Solid particle foam nucleators increased the thickness of the tube and foam extent of the final products when compared to chemically nucleated samples. PTFE powder seemed to be the most effective nucleator, probably because of the low surface energy interface where nitrogen nucleates. The result is consistent with contact angle theory (Young equation) on solid surface [50], where the spreading of gas phase on low surface energy solids is facilitated. The difference in cell size was not remarkable. Particle nucleators increased the uniformity of the foam composition and the density of cells, which can be seen in Figure 46, i.e. the cells are more densely packed.

Masuda et al. [62] studied the effect of small particle fillers on the elastic behaviour of polypropylene. It can be concluded that the amount of the fillers in this experiment is less than 1 % of weight and thus affects polymer elasticity only fractionally.
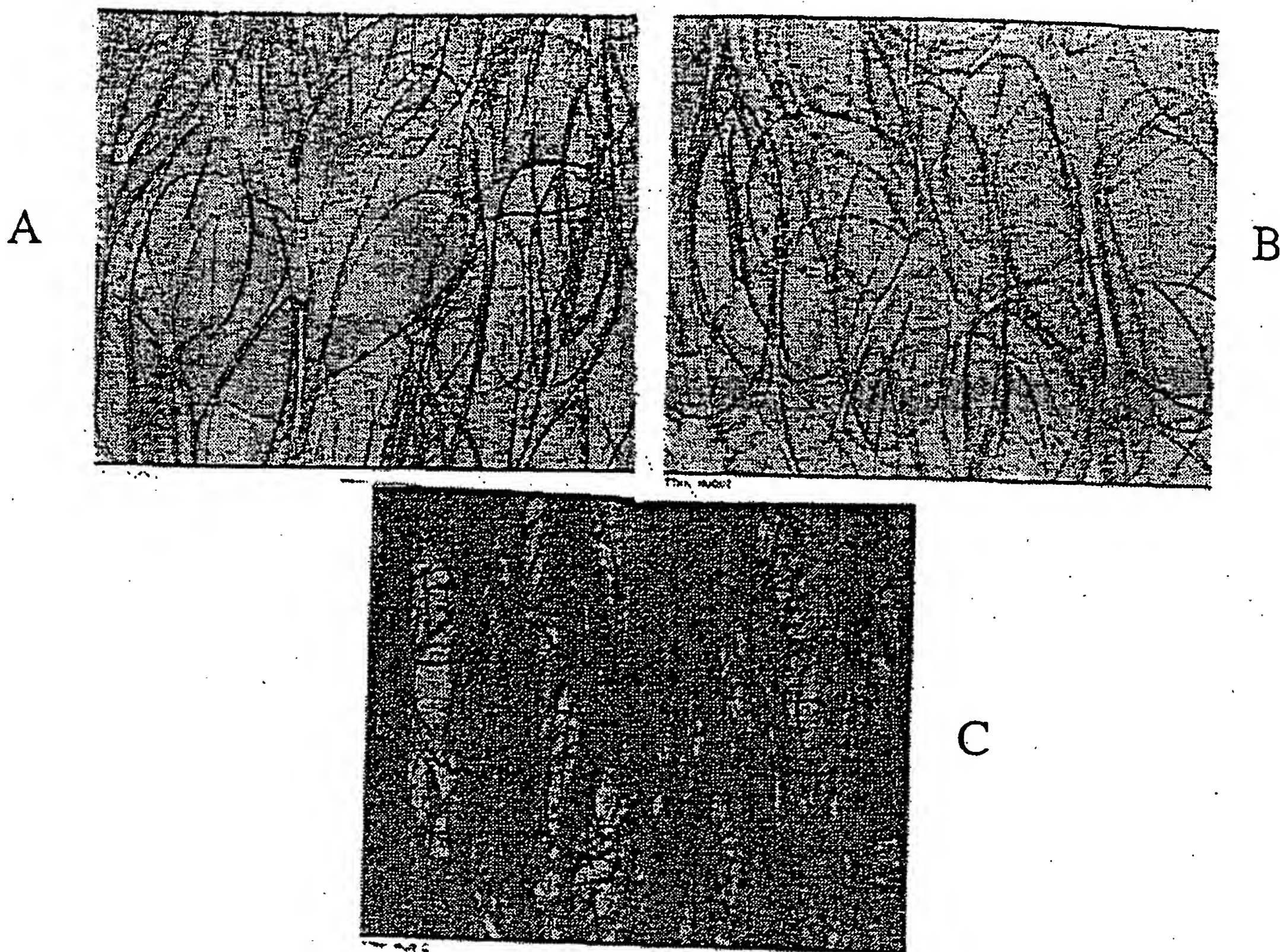
Figure 46. The packing of lenslike cells when particle and chemical nucleators have been used in processing of biaxially oriented foam film.
A) Foamed polypropylene
B) Foamed polypropylene + Talc powder
C) Foamed polypropylene + PTFE powder

3.6 Foam Studies with a Flat Film Die

An industrially interesting target for foamed films would be extrusion coating. After the experience of film blowing some studies were also done with Cloeren 5 layer flat extrusion die. A multimanifold die AABCC was used, where A and C extruders formed the skins and the middle layer (B) was foamed. Same PP-quality was used in all layers. The melt strength of the polymers was even more critical in extrusion coating and the viscosity of the blown film polypropylenes was too high for technology used in flat film extrusion. Some extrusion coating

grades were also tested, but the foam extent was very low immediately after die exit.

The demands in polymer foaming to high foam extent can, after these tests be assumed to be high viscosity and high melt strength. High viscosity inhibits the gas penetration through the bubble walls and melt strength allows thin walls.

For flat sheet die systems this foaming method might work perfectly, if the pressure inside the die could be increased sufficiently to avoid foaming inside the die, which causes the rupture of the surface. Figure 47 illustrates the common neck in behaviour in flat die extrusion. The waving phenomenon in Figure 48 was typical in foam studies with flat film die. The film is spread in a transverse direction causing waving ("neck out") because of three dimensional expansion of the foam bubbles in die exit. One way to control the waving is to support the extrudate on a cooled surface i.e. spreading the film in transverse direction with the aid of an extra roll or extruding the melt straight on a cooling roll or into a roll nip immediately after the die lip.

Running speed has to be kept low, since extension in bubble growth is too high for the film to bear line speed stretching. All the stretching occurs in temperatures higher than melting point, and it is well known that the extensional viscosity is increased if partly crystalline polypropylene is first crystallised and reheated into orientation temperature. In orientation the elongation of polypropylene is first dominated by necking and afterwards by strain hardening [41, 70].
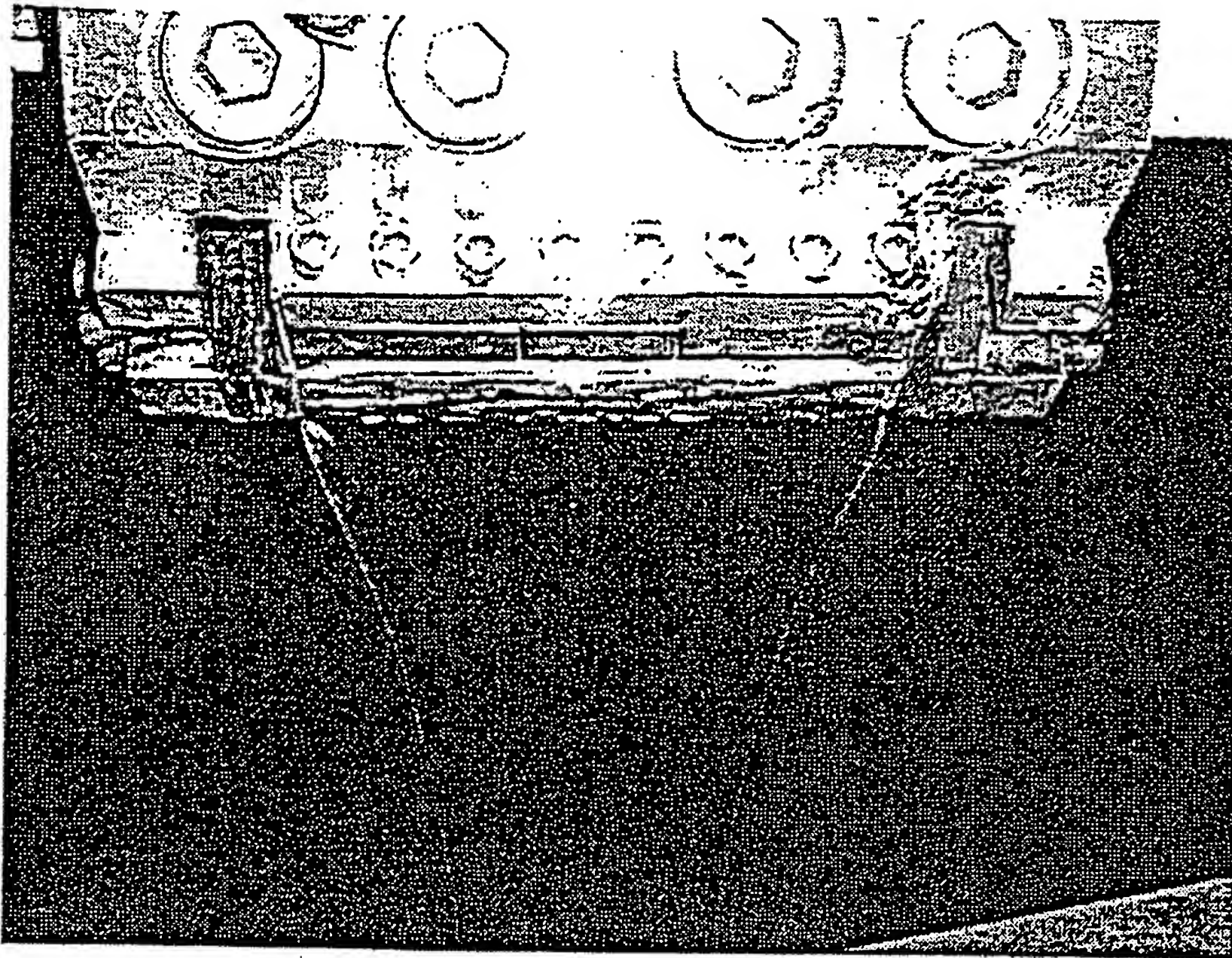
Figure 47. Solid film in flat die extrusion.
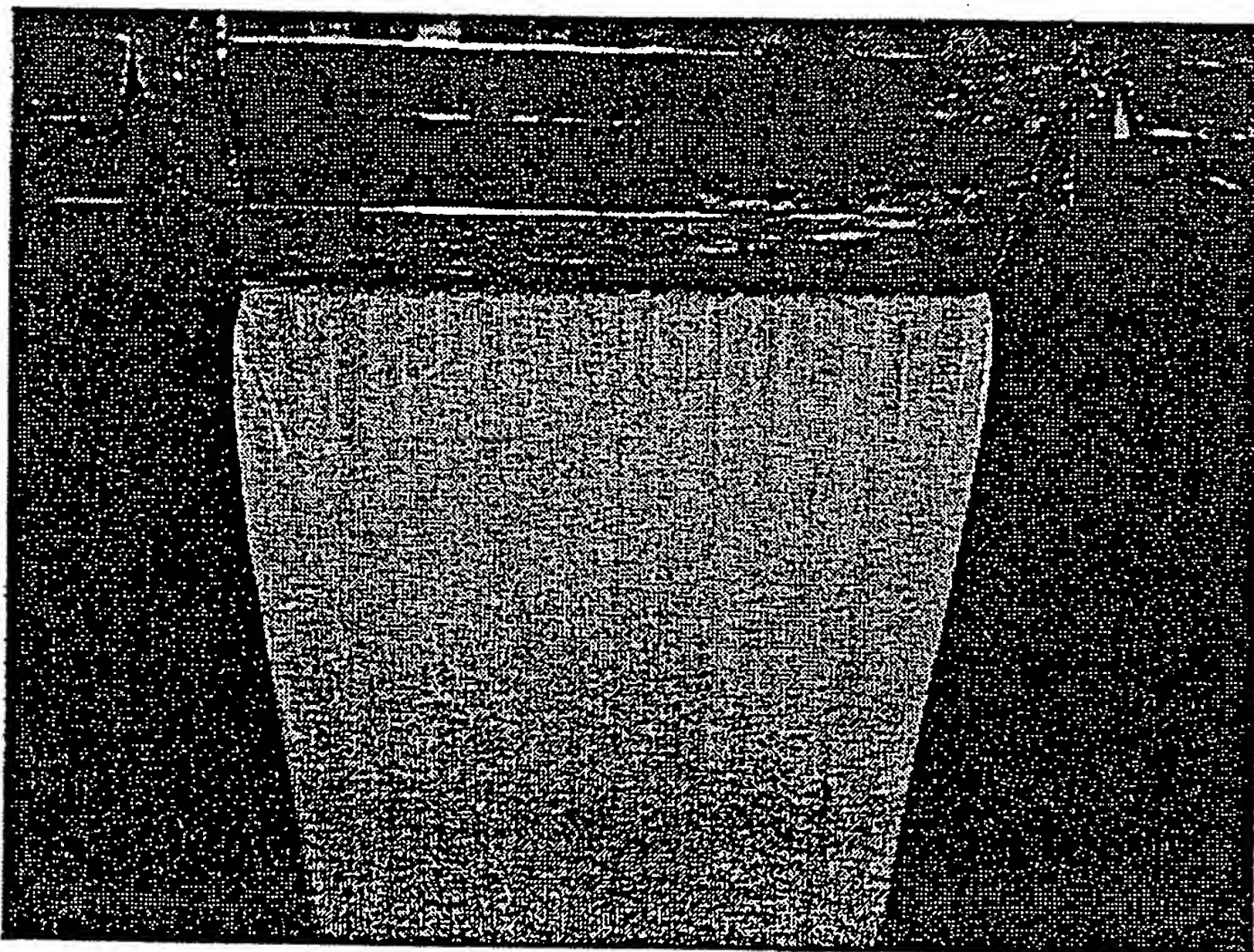
Figure 48. Foam film in flat die extrusion.

3.7 A Summary of the Experimental Results, Applications and Further Interests

Table 8 briefly summarises the results obtained in extrusion foaming. Processing conditions according to this study were strongly temperature control oriented and screw and die design played an important role in achieving a microcellular foam polypropylene. Biaxial stretching attested the problems inherent in temperature homogeneity of foamed structures and the difficulty in extension.

Table 8. A summary of the effect of polymer, different additives and technology on foam structure.
*   *low quality*
***** *high quality*

	Foam quality
Homopolypropylene (HomoPP)	* *
Polypropylene copolymer (CopoPP)	*
Bimodal polypropylene (BimoPP)	* * * * *
Exothermic nucleating agents	* *
Endothermic nucleating agents	* * * * *
Nucleating agent powder (100 %)	* * * *
Nucleating agent masterbatch	* * * * *
Particle nucleators	*
Nitrogen	* * *
Nitrogen / Helium (95/5 %)	*
Chemical foaming	* * *
Physical foaming with chemical nucleators	* * * * *
Chemical + particle nucleators	* * * *
Chemical nucleators+ PTFE powder	* * * * *
Circular die with internal mixing	* * * * *
Flat die	*

The principle of the three layer rotor die can be applied in foamed tube, sheet or film production. The idea to homogenise the flow history was successful and linked with improved thickness control and with high melt strength materials high foam extent products are attainable.

Foamed tube can be cut and opened from one side into a foam sheet, which can be used in thermoforming to produce deepdrawn cups and trays (Figure 49). The base idea in general would be to replace polystyrene in many applications with more environmental friendly and temperature resistant PP. High melt strength properties and heating on both sides during thermoforming of foamed PP are essential in order to avoid injurious corner thinning. For test drawing, a thermoforming unit with only one side heating was used and corner thinning could be discovered. BimoPP evinced much better drawing properties in thermoforming, which affirms the results from tension stiffening of entangled polymers.
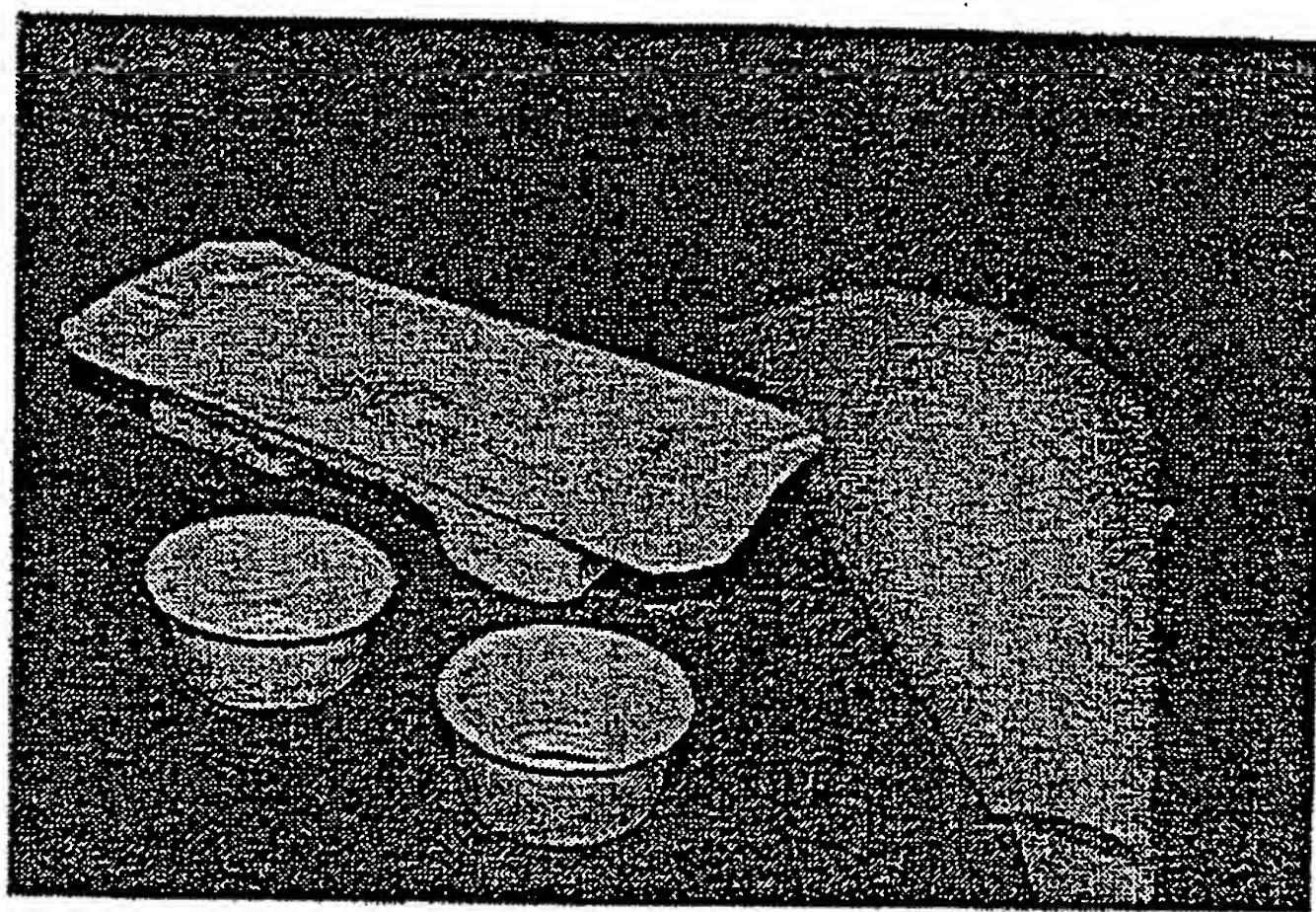
Figure 49.   Thermoformed products and a sample of BOPP foam film.
BimoPP

The biaxially oriented foam film studies presented here initiated an extensive program in VTT to utilise foamed OPP film in new applications, sensors and actuators. Permanent electric charge is injected by corona treatment inside the foam film to produce an electret. The electric charge is stored on foam bubble surfaces more effectively compared to solid electret films. Corona treated film

is used for self adhesive posters, labels and calendars, which can be placed on any surface and removed without any tapes or adhesives.

Electromechanical film is an oriented foam film with permanent electric charge, and it is metalled on both sides (Figure 51). When it is exposed to a mechanical or acoustic force, EMF film generates a voltage which can be measured and the film functions as a sensor (Figure 50). Conversely, when electric voltage is led between the electrodes, the film vibrates and produces sound, thus functioning as an actuator. The film is very sensitive in applications such as microphones, sensors to measure movement (safety floors, keyboards) and flat loudspeakers.
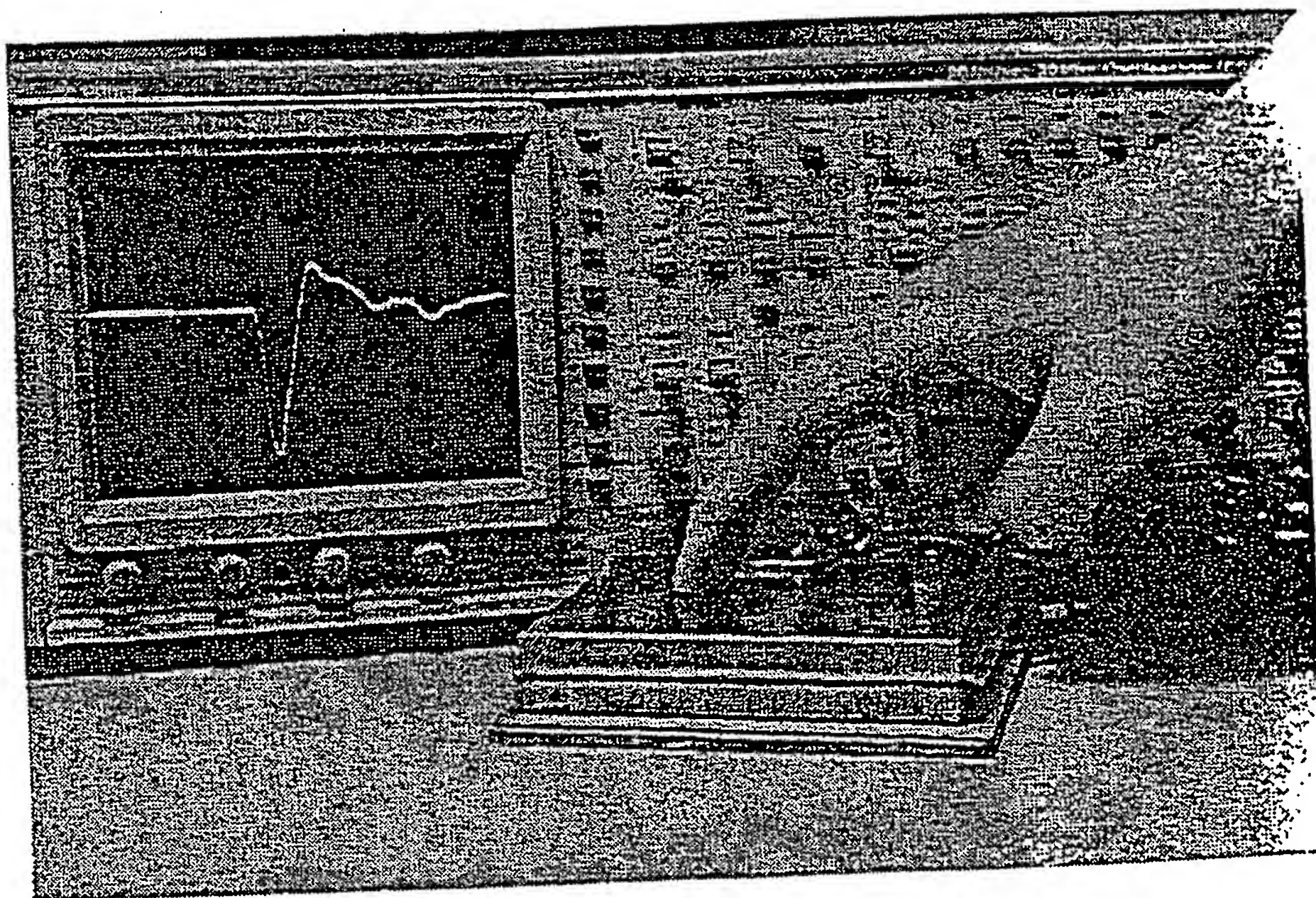
Figure 50. Permanent electric charge in BOPP foam film functioning as a sensitive sensor between two metal plates.
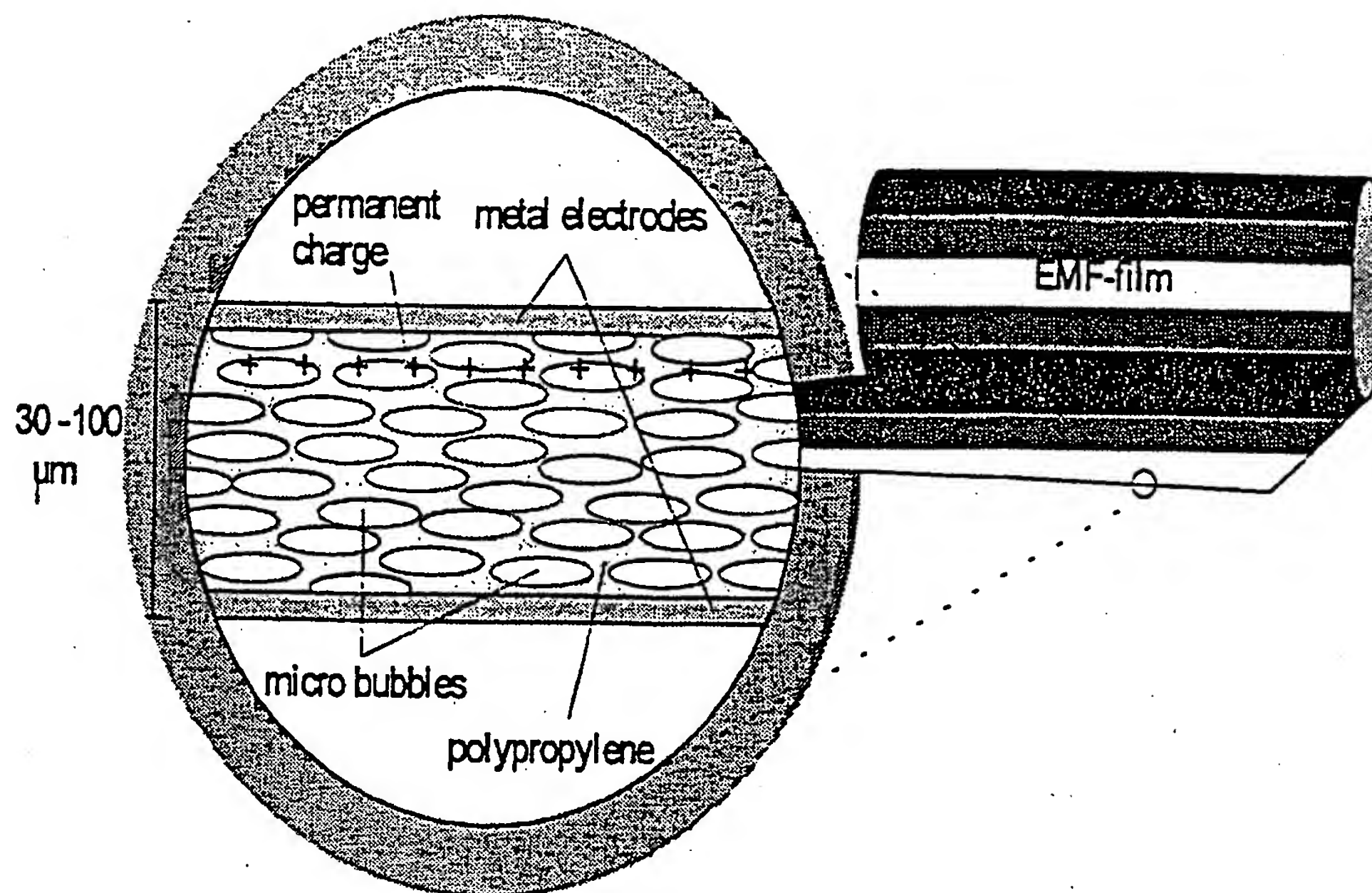
Figure 51. The principle of EMF (Electro Mechanical Film), where a permanent electric charge is stored on cell wall surfaces to produce an electret.

4. CONCLUSIONS

A new three layer blown film die design was developed to produce foamed tube and biaxially oriented PP film. The base idea of the die, to destroy and homogenise flow history before die exit, was successful.

The consequence of testing three different kinds of polypropylenes (homopolymer, bimodal polymer and copolymer) was that bimodal polypropylene with high melt strength properties was appropriate for extrusion foaming. The foam extent of the final product increased up to 70 - 80 %, but remained around 50 % with other types.

An endothermic foam nucleating agent was most applicable to produce a homogenous foam. Dozing of the agent was 0.1 to 0.15 %, which was sufficient to produce a low density structure together with physically compressed nitrogen as a foaming agent.

The effect of temperature was found to be most critical in extrusion foaming, where the temperature setting had to be defined with decomposition temperature of the foaming agent and polymer temperature to favour expansion in die exit to form a uniform microcellular foam structure. The moment when the dissolved gas expands and pressure is released is the most critical. By extensive experimental studies both with rheometer and extrusion pilot line, a correlation was found in theories of entanglement linked with high molecular weight end of molecular weight distribution to high melt strength properties governing a successful foaming in extrusion. Obvious connections can be found in determining the phenomenon in foam expansion and film blowing.

Biaxial film orientation of foamed tube was a challenging extension to this foam study and was something where on which no literature could be found. The most serious trouble was caused by the nature of a foam structure, which is insulating and which should be homogeneously cooled and reheated in setting temperatures in a short period of time. A cooling system and reheating oven were developed for this particular purpose.

The study also indicated the crucial importance of extrusion technology, which here means pressure and temperature control and also screw and die, which should be designed and focused in foaming and foam stabilising.

The studies presented here were goal-oriented, and can be comprehended a kind of pre-step into innovative applications in the field of EMF film for sensors, loudspeakers and self adhesive film applications, which are all further commercialised.

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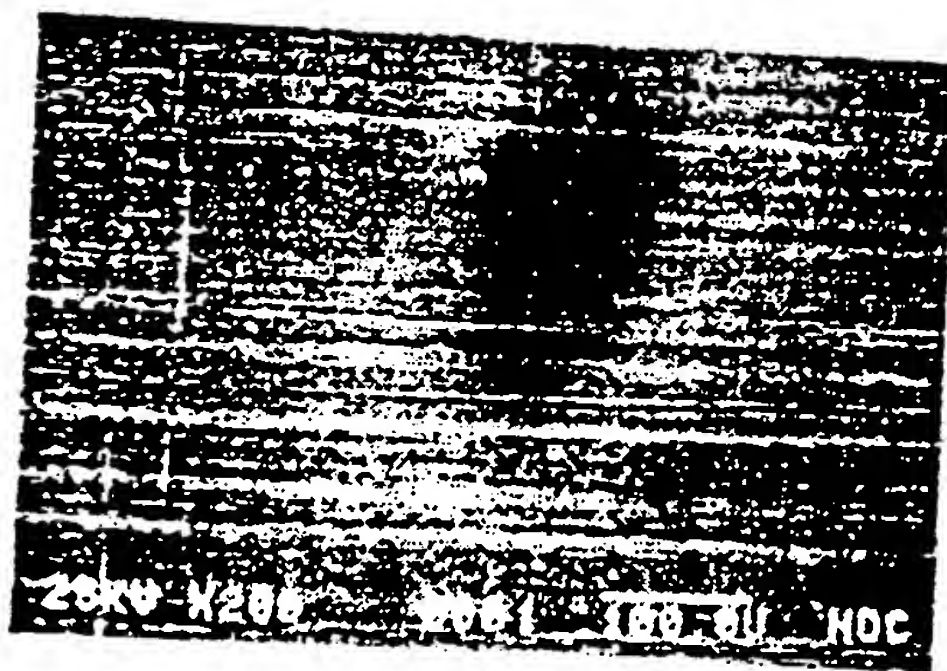
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[Fig. 3]

[Fig. 4]

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